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OHIO RIVER VALLEY STUDY
Sites, Methods, Data Summary for 1980

Volume 1. Main Report

by

R. W. Shaw and R. J. Paur
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

and

T. Royal
Mead Technology Laboratories
Research Triangle Park, North Carolina 27709

Contract 68-02-3288

Project Officer

R. K. Stevens
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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This report describes procedures for site location and for station preparation, operation, and periodic audits. Data summaries are presented for the period May through December 1980. Measurements included atmospheric concentrations of nitrogen oxides, sulfur dioxide, ozone, and peroxyacetyl nitrate; local meteorology; aerosol mass and composition; total suspended particulate; and precipitation. Special analyses for speciation of sulfur aerosols began in December 1980. Measurements of nitric acid and ammonia were made during the summer of 1981; results will be presented in a subsequent report.

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Site study and selection were performed under Grant R-805812 by Battelle Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. The stations were prepared under Contract 68-02-2566 by Northrop Services, Inc. - Environmental Sciences under the sponsorship of the U.S. Environmental Protection Agency. The data (except for particulate sulfur measurements) were collected under Contract 68-02-3288 by Mead Technology Laboratories under the sponsorship of the U.S. Environmental Protection Agency. Particulate sulfur measurements were performed by the Oregon Graduate Center under Cooperative Agreement CR807654 with the U.S. Environmental Protection Agency. The stations were audited under Contract 68-02-3285 by Northrop Services, Inc. - Environmental Sciences under the sponsorship of the U.S. Environmental Protection Agency.

This report refers to data collected during the period May 1, 1980 to December 31, 1980.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AGL	-- above ground level
EC	-- electron capture
EMSL	-- Environmental Monitoring Systems Laboratory
ESRL	-- Environmental Sciences Research Laboratory
FPD	-- flame photometric detector
GC	-- gas chromatography
GPT	-- gas-phase titration
hi-vol	-- high-volume
MTL	-- Mead Technology Laboratories
NBS	-- National Bureau of Standards
NMHC	-- nonmethane hydrocarbons
NSI-ES	-- Northrop Services, Inc. - Environmental Sciences
ORV	-- Ohio River Valley
PAN	-- peroxyacetyl nitrate
QAD	-- Quality Assurance Division
RAPS	-- Regional Air Pollution Study
TSP	-- total suspended particulate
UV	-- ultraviolet

SYMBOLS

b_{scat}	-- scattering coefficient
Z	-- atomic number

TYPING GUIDE SHEET

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This study was made possible by the skills and dedication of the station operators, Russell Arey, David Morehart, and Mark Sears of Mead Technology Laboratories (MTL). Daniel Strait (MTL) assumed management of the program during several months in 1981.

Joseph Williams of Northrop Services, Inc. – Environmental Sciences (NSI-ES) carried out the reconstruction of the experimental stations and setup and testing of the instrumentation, and took primary responsibility for station audits during the period of data acquisition. George Russwurm, Keith Kronmiller, Edward Tew, and Steven Lassiter (NSI-ES) also participated in station audits.

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(Battelle Columbus Laboratories) performed audits of the PAN analyzers during the summer of 1981.

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SECTION 1

INTRODUCTION

The energy crisis in the United States in the mid 1970's prompted the Federal Government and industry to develop a program of expanded use of the country's coal resources in energy generation. Recent research within EPA and the private sector has shown that such expanded use of coal may increase pollution problems. One geographical area particularly susceptible to such problems is the Ohio River Valley, where an exceptionally large increase in coal use has been contemplated. As of late 1979, new plants under construction or in the planning stage were projected to have more than 12,000 megawatts of generating capacity, mostly by coal-fired boilers. The impact on this Air Quality Control Region from such an increment in coal burning, while suspected to be of concern, could not be quantitatively predicted with any confidence.

The Ohio River Valley (ORV) Study was intended to gather data to measure trends in air quality as the coal-fired power plants went into operation. Specific pollutants that were measured included not only the criteria pollutants but also HNO_3, PAN, and primary and secondary organics, nitrates,[1] and sulfate. A major initial objective was to collect air quality data before, during, and after a 4- to 5-year period in which new coal-fired power plants were to be constructed and placed in operation in the ORV. Resource limitations,

however, prevented operation of the stations for the requisite 4- to 5-year period and allowed only 16 months of continuous operation. As a consequence, the study goals were revised to the following:

1. To develop, through source apportionment modeling techniques,[2] first estimates of the contribution of coal-fired power plants to ambient aerosol in the ORV;

2. To estimate the impact of coal-fired power plants and other industries on aerosol concentrations in the ORV during periods when fine particle masses were considerably above mean concentrations; and

3. To provide an ORV data base (including aerosol mass and elemental, organic, and ionic composition; acidity and ionic composition of precipitation; scattering coefficient; and gas-phase concentrations of SO_2, O_3, PAN, HNO_3, and NH_3) to aid future studies of the rates of transformation of sulfur and nitrogen compounds and studies of the deposition of these compounds.

The project included four separate tasks:

	Task	Contractor	Date Awarded	Date Complete
1.	site selections	Battelle Columbus Laboratories	9/79	1/80

	Task	Contractor	Date Awarded	Date Complete
2.	station preparation	Northrop Services, Inc. - Environmental Sciences	9/79	3/80
3.	station transport and operation and preliminary data compilation	Mead Technology Laboratories	9/79	9/81
4.	station quality control and sample analysis	Northrop Services Inc. - Environmental Sciences	1/80	9/81

The site selection involved choosing a region west of, a region in the midst of, and a region east of the main concentration of power plants in the ORV where effects from local urban and industrial sources would be minimal. Three St. Louis RAPS stations were renovated, new sampling systems designed and installed, new air monitors purchased and installed, and data acquisition systems purchased and installed that were suitable for later data analysis using existing EPA and contractor computing systems. The stations were transported to the sites in March 1980. The quality control program included six audit trips per year to each site by an instrumented mobile laboratory. During the audit, station instruments and procedures were checked. The sample analysis program included analysis by current techniques of fine and coarse

aerosol fractions from dichotomous sampler filters for: elements heavier than Mg, $SO_4^=$, NO_3^-, NH_4^+, H^+, and organic and elemental carbon.

This report presents the procedures and results of site selections, station preparation, station operation and audit, and sample and data analysis. Data summaries are presented from the start-up period, April-May 1980, through December 1980. Future reports will present data from subsequent periods and results of analysis of these and earlier data sets. Although we present some results and discussion of the data analysis, these are not intended to be complete but, rather, to suggest future lines of inquiry.

SECTION 2

SUMMARY OF RESULTS AND CONCLUSIONS

This section presents (1) an outline of the present form of the data obtained during 1980, (2) tentative conclusions concerning the applicability of the ORV data to the goals stated in Section 1 of this report, and (3) conclusions from some initial analyses of the 1980 data.

The current status of 1980 data is presented in Table 2-1. The data available from the first group of continuous monitors are in the form of hourly averages and their means, maxima, and various percentiles. The aerosol data from dichotomous samplers consist of the atmospheric concentrations of mass and abundances of the elements with $Z > 12$. The aerosol samples are in storage and are available for future analysis using more specific techniques such as electron microscopy, X-ray diffraction, extraction and chemical analysis, etc. The precipitation analyses were for pH and concentrations of NH_3^+, NO_3^-, and $SO_4^=$; although these data are available, the quality control editing and several adjustments have not been made as of this writing.

The ORV Study has provided a data base from rural sites for the period May 1980 through August 1981. The data include aerosol mass and composition,

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TABLE 2-1. STATUS OF 1980 DATA

Measurement	Time Period	Availability
NO_x	May through December	hard copy
O_3	"	9-track magnetic tape
SO_2	"	
b_{scat}	"	
temperature	"	
barometric pressure	"	
wind velocity	"	
dew point	"	
solar radiation	"	
fine and coarse aerosol mass and elemental composition	May through December	hard copy Hewlett-Packard disc
TSP	May through December	hard copy
wet precipitation	"	
PAN	September through December	hard copy
particle sulfate speciation	December	hard copy Hewlett-Packard disc
NH_3	not on line in 1980	
HNO_3	"	

gaseous pollutants, and local meteorology. These data are suitable for use in chemical element balance calculations and in other schemes for source

apportionment. The period is not long enough to determine the presence of systematic trends in atmospheric concentrations; we estimate that a period of at least 3 years is necessary to test for trends in the presence of a 1-year cycle.[3] The data do, however, provide a benchmark against which future measurements can be compared in assessing the impact of new sources and control strategies. These data also provide the opportunity of measuring the chemical species present during various meteorological and other episodes, several of which are discussed in Section 4 of this report.

In preparation for subsequent data analysis, the air quality data were examined for consistency, gaps, patterns, and other characteristics that could guide source apportionment modeling. Conclusions of this preliminary examination were:

1. Pollutant concentrations (gases and particles) averaged over the period May through December 1980 are approximately the same at all three sites. This indicates that the air mass was relatively homogeneous over the three sites and that local sources did not cause large differences from site to site. We infer that our data are indeed representative of atmospheric concentrations over a large region, and that source apportionment may provide information about contributions to regional (not merely local) air quality.

2. Significant temporal correlations exist for aerosol compositions among the three sites. This result is consistent with Conclusion 1.

3. Aerosol mass data from 12-h samples taken May 14 to August 14, 1980 reveal no diurnal patterns for mean mass values nor for mass distribution shapes. Apparently 12-h periods are too long to provide information on times for formation and decay of aerosol concentrations. Fortunately, as discussed later in this report, additional instrumentation provided semicontinuous measurements of sulfate concentrations.

4. The fine mode aerosol consisted mostly of sulfate with a very small contribution of lead. The coarse aerosol composition is consistent with that of crustal shale and limestone. X-ray diffraction of aerosols collected at the center station during three days in August 1980 showed that the major crystalline components in the coarse fraction were quartz and calcite; mullite, an unambiguous marker for fly ash, was detected in one sample. Major crystalline components in the fine fraction were mascagnite [$(NH_4)_2SO_4$], koktaite [$(NH_4)_2Ca(SO_4)_2 \cdot H_2O$], and kaolinite. These results show that aerosols collected in these rural areas are similar to urban samples--the fine fraction is dominated by sulfate--and demonstrate that industry contributes significantly to atmospheric concentrations over a large, rural region.

5. Relative levels of potassium and iron were much higher in the fine mode aerosol than in the coarse. Light absorption of fine aerosols was strongly correlated with potassium but not with sulfur. High levels of potassium and strong light absorption indicate combustion processes. The relative contributions of industrial, agricultural, and residential combustion remain to be determined.

6. Average concentrations of nitrogen oxide were dominated by relatively brief events; gaseous sulfur concentrations were affected to a lesser extent by events and nitrogen dioxide even less so.

7. The distribution of sulfur between gas and particle phases changed markedly with season, with the lowest particle fraction occurring during the winter. This effect is apparently due to lower gas-to-particle transformation rates during the colder, shorter winter days. These observations indicate the importance of seasonal effects on the distribution of materials in the atmosphere.

8. Levels of PAN at the three sites never exceeded 0.5 ppb during the measurement period. It appears that only small concentrations of nitrate were present as PAN at the ORV sites.

SECTION 3

METHODS

SITE SELECTION

Recommendations for the sites were made by C.W. Spicer and coworkers of Battelle Columbus Laboratories. Their recommendations were based on a review of existing data from the ORV and an airborne survey of potential sites.[4] The region of interest as specified by EPA was along the ORV from the intersection of Illinois, Kentucky, and Indiana to the intersection of West Virginia, Ohio, and Pennsylvania. Three sites were to include one near the western (upwind) end of the region, one located in the center of the region, and one near the eastern end. These sites were to be removed as much as possible from local emission sources, especially power plants, highways, and urban areas. A detailed report of the site selection appeared in an informal project report to EPA; a brief summary follows.

Review of past air pollution data from the Sulfate Regional Experiment indicated that utilities along the ORV are an important source of SO_2 in the Eastern United States and contribute most of the NO_x emitted in the ORV. Similarly, industries contribute most of the TSP in the Valley.

Weather in the ORV is such that transport of pollutants up the Valley prevails except during the winter. Annual prevailing wind directions show that transport into the Valley is from the south, and that the surface winds become southwest as they pass over the Valley and into the Northeastern United States. Using the work by Holzworth,[5] Spicer and coworkers point out that the mean morning mixing height over the western part of the ORV is below 500 m, which indicates a tendency for overnight accumulation of pollutants.

Power Plants

The candidates for the western site were chosen to be upwind of the high concentration of power plants located along the Wabash River between Indiana and Illinois and to be out of the plume from large power plants around Paducah. Candidates for the intermediate site were limited to the area where Indiana, Kentucky, and Ohio join because new ORV power plants are scheduled to come on line upwind of this region. It was necessary, however, to avoid the urban plume from Cincinnati as much as possible. The eastern candidate sites were chosen to be downwind of the prevailing winds from the lower ORV and to avoid plumes from Dayton, Columbus, and major highways.

According to a recent report that characterizes the emissions of major fossil-fueled power plants in the ORV,[6] the greatest power plant concentration is between Portsmouth, OH and Louisville, KY. In this region 45 coal-fired power plant boilers are in operation and 17 additional ones are planned. The areas of greatest generating capacity and planned increases in capacity are in the regions of Cincinnati and Louisville. The report presents characteristics

of and emissions data from power plants chosen as representative of the ORV (Table 3-1). The sample power plants range from quite new ones with relatively high generating capacities to rather old ones. The emissions as shown in Table 3-1 are based on approximately 10 measurements at each plant. These data show that most of the emissions consist of SO_2 and NO and that particle emissions are considerably lower. It is interesting that particulate sulfate emissions are quite low for all plants and that H_2SO_4 emissions are significantly higher in plants with SO_2 scrubbers. The scrubbers, however, are apparently very effective in removing the acid halogen gases. Elemental analysis of particles collected in cascade impactors showed that, for the three plants without SO_2 scrubbers, particles below 10 μm in diameter consisted mostly of Si, Al, Fe, Mg, and K (in that order) and S was only a trace component of these particles. Particles from the two plants with SO_2 scrubbers consisted mostly of S, Si, Al, and Fe. In plant D, S was 20 times higher than any other element.

We infer from these data that most of the atmospheric particles expected from the power plant emissions will be oxidized, secondary particles from SO_2 and NO. Primary particles, including aluminum silicate fly ash, are expected to be present in much smaller amounts.

Airborne Surveys

After choices were made based on the considerations outlined above, topographical maps were examined to select areas free from nearby point sources, with uniformly level terrain, and with accessibility to electric power. The

TABLE 3-1. REPRESENTATIVE FOSSIL-FUELED POWER PLANTS IN THE ORV[a]

Plant	Characteristics			Emissions (kg/h)							
	Age (years)	Capacity (MW)	Controls	I.P.[b]	F.P.[c]	particulate $SO_4^=$	H_2SO_4 mist	SO_2	NO	HCl	HF
D	3	411	particles SO_2	120	66	2	69	2800	680	2.6	<0.3
A	11	560	particles	380	100	<0.3	14	3600	3000	250	22
E	19	156	particles SO_2	43	24	0.4	30	1000	650	<0.2	<0.2
C	23	163	particles	240	67	-	2	1400	390	68	6
B	27	125	particles	14	7	<0.1	6	1000	390	41	4

[a]Data from Reference 6.

[b]Inhalable particles (equivalent aerodynamic diameter of <15 μm).

[c]Fine particles (equivalent aerodynamic diameter of <2.5 μm).

best remaining candidate sites were then explored by airborne monitoring survey.

Airborne surveys were made over an area of 400 km^2 around each candidate site. East-west traverses were made at intervals of 5 km and altitudes of 300 m AGL. Continuous measurements were made of O_3, NO_x, b_{scat}, SO_2, and temperature. Samples were also taken for subsequent analysis for PAN, NMHC, NO_3^-, and $SO_4^=$. Vertical profiles were taken to check uniformity of pollutant concentrations with altitude. The investigators inferred the relative importance of local emission sources from the degree of homogeneity in pollutant concentrations over the 400-km^2 areas. Those sites least affected by local sources were considered to be the most representative of regional air quality.

The candidate sites were surveyed under a variety of wind conditions based on the prevailing winds in the ORV. Four flights were made over the area later selected as the western site, nine flights over the central site, and nine flights over the eastern site. Altogether, data were reported from 38 grid traverses over candidate sites during October and November of 1979. Based on these results, recommendations for the three sites were made by Battelle and accepted by EPA. Site locations are shown in Figure 3-1.

Site Locations

The West station is in Union County, KY, 10 km west of the city of Morganfield on Route 56. The station coordinates are Lat 37°41'N and Long

Figure 3-1. Geographical relationship of the three ORV monitoring stations.

88°01'W. It is located in a rural farming community and is approximately 130 m west of the nearest public road.

The Center station is in Franklin County, IN, near Route 101 and 10 km north of Brookville. The station coordinates are Lat 39°28'N and Long 84°56'W. It is located in a rural farming community and is 40 m west of the nearest public road. (The Center station is 330 km and 250 km from the West and East stations, respectively.)

The East station is in Ashland County, OH near Route 97 and 11 km southwest of Loudenville. The station coordinates are Lat 40°36'N and Long 82°19'W. It is located in the Mohican State Forest.

INFORMATION FROM COUNTY SOIL SURVEYS

West Station: Union County, Kentucky[7]

The mean January and July temperatures are 1°C and 25°C, respectively. The growing season is mid April to late October. The average precipitation is 117 cm, of which about 50% falls during the growing season. Average snowfall is 36 cm. On an average of 7 days, at least 2.5 cm of snow is on the ground. The percentage of possible sunshine is 75% in summer and 45% in winter.

Soils surrounding the West station are of the Memphis series. They are deposited by the wind, of medium acidity, and brown.

Center Station: Franklin County, Indiana[8]

The climate of Franklin County is humid and temperate. The mean January and July temperatures are -1°C and 24°C, respectively. The winters are characterized by sudden temperature changes. The average growing season is late April to mid October--dates, respectively, of the last spring killing frost and first fall killing frost. Mean annual precipitation is 100 cm, of which about 52% falls during the growing season. Much of the rainfall during spring and summer is associated with cyclonic storms. High wind speeds are infrequent and tornadoes are rare. Before agriculture began, nearly all the county was covered with deciduous trees; most is now in cropland or pasture.

Soils surrounding the Center station are of the Russell and Fincastle series which developed as calcerous Early Wisconsin glacial drift. Their pH ranges from 5 to 6 (strongly acid to acid) because of past leaching of free lime carbonates to a mean depth of 45 m. The Russell soils are brownish-yellow and the Fincastle are brownish-grey.

The soil parent materials are composed of underlying bedrock including a large portion of limestone as well as quartz, granite, schist, gneiss, etc. transported by Early Wisconsin glaciation from the north.

East Station: Ashland County, Ohio[9]

The mean January and July temperatures are -4°C and 22°C, respectively. The growing season is from late April to mid October. The average precipitation

is 93 cm, of which 60% falls during the growing season. Percentage of possible sunshine is 65% in summer and 40% in winter. Severe thunderstorms and tornadoes occur occasionally.

Soils surrounding the East station are of the Lordston-Berks series. This region was not glaciated and the soils formed mainly in weathered sandstone. The soils are strongly acid and are dark greyish brown at the surface.

STATION PREPARATION

Three stations from the St. Louis RAPS[10] were refurbished and provided with new instrumentation. Station preparation, initial checkout, and operator training are described in detail in Appendix B; a brief summary follows.

Each station consists of a metal building that measures 4.9 m x 3.3 m, is 2.7 m high, and has electric heat and air conditioning. Continuous air monitors and sample collection devices are listed in Table 3-2. The data acquisition system is a scanning digital voltmeter interfaced with a desk-top computer. Instrumentation is arranged to provide convenient access for calibration and repair and to avoid cross-contamination from the outlet of one device to the inlet of another. Several special design features are described below.

TABLE 3-2. STATION EQUIPMENT

Function/Instrument/Parameter Measured		Instrument Manufacturer	Instrument Model
continuous gas monitoring	sulfur	Meloy	SA285E
	NO_x	CSI	1600
	O_3	Bendix	8002
aerosol measurements	dichotomous sampler	Beckman	
	high-volume sampler	Kurz	
	integrating nephelometer	MRI	1591
	continuous sulfate species	(by Oregon Graduate Center)	
data acquisition	digital voltmeter	Eastchester	
	desk-top computer	Hewlett-Packard	9825
meteorology measurements	temperature	Climetronics	100087
	pressure	Climetronics	100091
	wind speed	Climetronics	100108
	wind direction	Climetronics	100161
	dew point	Climetronics	100089
	solar radiation	Climetronics	100241, 100507
special sampling		Method	
	gaseous and particulate organic compounds	collection and subsequent chromatographic analysis	
	PAN	on-site gas chromatography	
	wet precipitation	collection and subsequent ionic analysis	
	HNO_3	collection and subsequent chromatographic analysis	
	NH_3	collection and subsequent chromatographic analysis	

Gas Monitor Sample Inlets

Individual filtered and heated Teflon inlet lines are provided for each gas analyzer. These lines avoid the condensation and accumulation of dirt which occur in standard glass manifolds and the assembly was designed to permit the

passage of calibration gases through the sampling lines. Design details are presented in Appendix A.

Data Acquisition System

The choice of a digital voltmeter linked to a desk-top computer was based on: (1) the desirability of data tapes which are compatible with contractor and EPA data reduction computing facilities; (2) the possible need for changes in the data acquisition program during the course of the study, and (3) the need for rapid repair or replacement in case of system failure. The Environmental Sciences Research Laboratory has a Hewlett-Packard 9845 computer with tape and disc drives, CRD, and flat-bed plotter graphics. Use of a desk-top computer permits straightforward alterations in the data acquisition programs and, because of the nationwide sales volume of these devices, relatively fast repair or replacement service. Based on the foregoing considerations and a comparison of the costs of alternative data acquisition systems, instrument packages were purchased from Eastchester Corporation that consist of a Hewlett-Packard 9825 desk-top computer with real-time clock interfaced with a digital voltmeter to permit input of 16 channels of analog data. The system has a battery back-up power supply which can maintain operation in the event of line power failures for up to 6 h.

The data acquisition system scans all analog channels once per minute and calculates hourly averages from the scans. The record for each channel is compressed into a single five digit number such that the first two digits give the number of scans and the last three give the hourly average. The data

recorded on magnetic tape include site ID, date, time, number of scans, and hourly average.

Continuous Sulfate Measurement and Speciation

A flame photometric sulfur detector has been fitted with a special inlet system which uses a series of denuder tubes. The first tube removes sulfur gases and permits aerosols to pass into a switching valve which directs the airstream into one of a set of tubes maintained at just above volatilization temperature of the aerosol sulfate species to be removed. The instrument provides measurements for aerosols of sulfuric acid, ammonium sulfate and ammonium acid sulfate (together), and the remaining sulfates which are called refractory sulfates. A detailed description of the instrument is included in Appendix A of this report.

The instrument was conceived, designed, and built by Dr. James Huntzicker and colleagues at Oregon Graduate Center[11] and was installed in the Center station in November 1980. The instrument is microprocessor-controlled and data are stored directly on magnetic tape. Oregon Graduate Center analyzes and reports the data to EPA.

Precipitation Sampler

Wet precipitation is collected in a Pyrex funnel with collection diameter of 11.5 cm. The collected liquid passes through Teflon tubing into a Pyrex separation funnel with a stopcock so that individual drops pass through to the

collection vials. A photosensitive drop counter is set so that a quantity is collected equivalent to 0.25 cm of rain or 25 ml of sample. The sample vials are carried in a revolving sequential fraction counter and the entire assembly, except the collecting funnel, is contained in a refrigerator at 5°C. The sampler was designed and assembled by Dr. Greg Kok of Harvey Mudd College.

From the study start-up until March 1981, the collection funnels were always uncovered. Contamination from dry deposition was minimized by rinsing the apparatus daily with deionized water. During the week of March 16-21, 1981, automatic collector covering devices were installed which are triggered by wet precipitation. The automatic covering devices were designed and built by Keith Kronmiller of Northrop Services, Inc. - Environmental Sciences.

The samples are shipped at weekly intervals to the analytical laboratory in cold containers which maintain the sample temperatures near 0°C. Precipitation analysis is carried out by ion chromatography for $SO_4^=$ and NO_3^-, ion selective electrode for NH_4^+, and Grans titration and glass hydrogen ion electrode for H^+.

STATION OPERATION

Daily Maintenance

The field operators live near their sites and are responsible for operating each station and its equipment. The most centrally located operator is equipped

with a leased vehicle and is responsible for resupplying the stations with cylinders, standards, equipment, and supplies for maintaining the network.

During daily site operations the operator performs the following checks and operations:

1. Verify that the analyzers are in normal operation modes and functioning properly.

2. Perform a zero and span on each analyzer every day to insure the calibration and data validity.

3. Should the zero or span response at the analyzer indicate an error greater than ±3%, record the response and perform a zero and/or span adjustment.

4. Insure data capture by inspecting the data acquisition system's response to the zero and span, check this response for each analyzer, and review the response of the backup strip chart recorders. Review previous data for reasonableness, and place date/time data on each chart. Service the chart supply and magnetic tape as necessary.

5. Perform visual and quantitative checks on the meteorological gear.

6. If precipitation has occurred, transfer the precipitation sample for transport and subsequent analysis.

7. Service all particulate samplers, retrieving samples taken and/or preparing them for further sampling. Check dichotomous sampler impactor jets weekly for clogging.

8. Maintain the station and general area in a neat, orderly condition.

9. Observe the shelter integrity, i.e., that the shelter temperature is between 68-78°F and its physical condition is intact.

10. Monitor the amount of support and calibration gases. Upon initiating new compressed gases into service, check the lines, fittings, and regulators for leaks.

11. Check zero air system for needed service (repair or charcoal or desiccant replacement).

TYPING GUIDE SHEET

12. Check the level of deionized water in the zero air humidifier.

13. Execute special sampling/analysis (PAN, NH_3, etc.) as necessary.

14. Update the station's permanent log and visually check the security of all lines and signal connections.

15. Initiate maintenance to correct any deficiencies or to preclude possible areas of failure within station systems as recommended by the respective manufacturers of the equipment.

16. Document all maintenance performed in the permanent station record.

The calibration operation occurs (at 3-day intervals) every third working day. The calibrations carried out at each site are scheduled so that O_3 and NO_x analyzers are calibrated in the mornings, while the SO_2 analyzer and nephelometer are calibrated on the following day. In addition to the calibration of the measurement systems at each site, all regular daily procedures are followed. A general schedule of sampling and calibration intervals for the major measurement systems is listed in Table 3-3.

Instrument Calibration

The calibrator consists of mass flow controllers, mixing and reaction chambers, and a voltage regulator supplying power to the UV lamp to insure stability. It is capable of generating extremely low level (ppb) pollutant concentrations and is durable for field use. Instrument calibration is carried out at 3-day intervals. The calibrations are consistent with EPA method requirements as specified in the Federal Register.[11a] The calibration materials are either NBS Standard Reference Materials or traceable to those standards.

TABLE 3-3. SAMPLING AND CALIBRATION SCHEDULE

Parameter	Sampling Frequency	Calibration Interval	Sites
Gaseous Pollutants			
SO_2	continuous	3 days	1,2,3
O_3	continuous	3 days	1,2,3
NO_x	continuous	3 days	1,2,3
Particulate			
dichotomous sampler	24-h sample daily	14 days	1,2,3
high-volume sampler	24-h sample every third day	30 days	1,2,3
integrating nephelometer	continuous	3 days	1,2,3
Special Sampling			
PAN	150 samples/year	when applicable	1,2,3
precipitation	when applicable	at time of capture	1,2,3
HNO_3	150 samples/year	before and after sampling period	at site(s) requested
organic compounds	150 samples/year	before and after sampling period	1,2,3
NH_4	150 samples/year	before and after sampling period	at site(s) requested
Meteorology			
wind direction	continuous	annual, when applicable	1,2,3
wind speed	continuous	annual, when applicable	1,2,3
temperature	continuous	annual, when applicable	1,2,3
relative humidity	continuous	annual, when applicable	1,2,3
barometric pressure	continuous	annual	1,2,3
solar radiation	continuous	annual	1,2,3

Calibration methods used during the study are dilution, UV photometry, GPT, calibrated flow orifice devices, and appropriate meteorological standards.

Cylinder pollutant gases are certified biannually by comparison to recent EMSL/QAD certified gases, to document the standard used to calibrate each analyzer. The ozone generator settings are verified monthly with a UV transfer standard that is biannually recertified through reference to MTL's primary UV photometer.

Metering valves for pollutant flows and calibrated mass flow controllers are used to establish the flow rates for each of the different gases and at the respective calibration levels. The calibration consists of zero air response and of air containing the pollutant at 5, 20, 50, and 90 percent of full scale on the operating range. The flow through each is checked at each concentration by an NBS traceable bubble flowmeter on the days of calibration. Should the site operator at the time of calibration find that the instrument error exceeds ±3% from the 90 percent calibration concentration, the operator adjusts the analyzer to reflect the correct zero and span response concentrations. This adjustment, the analyzer status, and the error are logged into the station records. When each analyzer undergoes routine maintenance or repairs, a four-point analyzer calibration is performed prior to resuming ambient measurements. The calibration is conducted using the same standards and a dynamic calibration unit using NBS standards and NBS traceable calibrated flow measurements at each concentration level.

Zero Air

The zero air for calibration of the SO_2 analyzer requires ambient concentrations of water and CO_2. This is achieved using compressed zero air with 320-350 ppm CO_2, with humidification accomplished in the station.

The zero air for the NO_x and O_3 analyzers is provided from the station's clean air supply. A UV lamp generating O_3 aids the cleanup process by converting NO to NO_2. The resultant NO_2 and O_3 are removed using soda lime/ charcoal and a molecular sieve train to provide a contaminant-free source of zero air. Both sources of calibration zero air are bubbled through deionized water to achieve a humidity level equivalent to the ambient air at the time of calibration. The calibration systems are composed of tubing, fittings, and valves of either Teflon, glass, or stainless steel, as dictated by pollutant compatibility.

Sulfur Dioxide

Air containing the pollutant at 5, 20, 50, and 90 percent of the 100 ppb range is prepared by dilution of measured amounts of NBS traceable SO_2 in N_2 gas contained in a treated aluminum cylinder. Each cylinder is fitted with conditioned stainless steel regulators for delivering the SO_2 (approximately 4 ppm) to the dilution systems. Zero air containing ambient amounts of CO_2 and H_2O (as previously mentioned) dilutes the flow of the pollutant prior to sampling by the analyzer. The flow rates are determined by bubble meter and recorded.

Ozone

Levels for the O_3 analyzer employ the use of a calibrated sliding sleeve shielding a UV lamp which ozonizes the air passing through the generator housing. This sleeve is calibrated with a certified UV transfer standard as outlined in the Technical Assistance Document Transfer Standards for the Calibration of Ambient Air Monitoring Analyzers for Ozone.[12] The pollutant flow is diluted by the humidified zero air source and introduced to the analyzer by a vented calibration line.

Oxides of Nitrogen

The oxides of nitrogen (NO and NO_2) analyzer is calibrated by GPT as outlined in the Technical Assistance Document Chemiluminescence Measurement of Nitrogen Dioxides.[13] An aluminum certified cylinder containing NO in nitrogen (traceable to NBS) is diluted and/or reacted accordingly during the calibration of the NO_x analyzer. The zero air source is the station's clean air system. The desired upper range concentrations are produced by reactive and dilution techniques. During each calibration, the converter efficiency is ascertained and documented.

Dichotomous Sampler

The dichotomous sampler is calibrated for flow rate every 2 weeks. The flow rate calibration is determined by a dry test meter traceable to NBS. During each calibration the low flow filter reject point is checked and adjusted as necessary.

High-Volume Sampler

The high-volume sampler is calibrated with a standard orifice flow device as described in the Federal Register.[14] The orifice device has been referenced by EMSL/QAD and used on a monthly basis to verify the flow character of the high-volume systems. The TSP method is performed using applicable quality assurance guidelines. Calibration systems are recertified annually at EMSL/QAD.

Nephelometer

The integrating nephelometer undergoes an electronic zero and calibration every third day. A three-point calibration using filtered air, a Freon-12 source, and a Freon-22 source was performed every 3 working days until late January 1981. At that time it was decided to use the Freon calibration once a month and to carry out the electronic check every 3 days. This decision was based on the tendency of nephelometers to fail catastrophically when failures occur; therefore, the electronic check is sufficient over short periods.

Meteorology

During each site visit, visual performance checks are conducted on the meteorology equipment. Observations are made regarding the reasonableness of data being collected at the time of the visit. Every 3 days a performance check is performed. At each performance check, the readings are recorded in the station journal without any adjustments or recalibrations unless an error trend is developing.

Repair and Maintenance of Equipment

The field operators are trained to perform maintenance and repairs on equipment in the field to the extent it does not interfere with normal network operation. The on-site operators are trained in diagnostic troubleshooting, first-level field repairs, and service procedures for each instrument located at their site. When the instruments fail and repair is not feasible in the field, the project manager decides either to transport the affected instrumentation to one of the repair facilities or to send a repair representative to the instrument site. The repair decision is based on the nature of the failure and the exact location of repair parts; the overall objective is to return the instrument to on-line status as quickly as possible. MTL purchased one additional NO_x analyzer to use as a spare during emergency repairs. Table 3-4 shows the routine maintenance performed at the sites.

Quality Control

Many aspects of a comprehensive quality control program for the parameters examined in the ORV Study overlap into the normal site operations and routine calibrations discussed above. An example is the routine calibration of the gaseous SO_2 analyzer. Since this occurs at 3-day intervals and is accompanied with full standardized forms, quality control with respect to this instrument's performance is accomplished in the frequent calibration procedure.

Initial quality control concerned the establishment of known and certified calibration and quality control devices and standards. All flow measurement

TABLE 3-4. PREVENTIVE MAINTENANCE SCHEDULE

Equipment	Service Performed					
	daily	30 days	60 days	6 months	12 months	24 months
Nitrogen Oxides Analyzer						
sintered stainless filter elements					REPLACE	
desiccant		REPLACE				
activated charcoal			REPLACE			
squirrel cage fan				OIL		
fan screen			CLEAN			
converter material					REPLACE	
Teflon filter		REPLACE				
Sulfur Analyzer						
rotameters					CLEAN	
vacuum pump					REBUILD	
H_2 regulator						REPLACE
FPD optical window					REPLACE	
FPD exhaust filter				REPLACE		
fan air filter					CLEAN	
Teflon filter		REPLACE				
Ozone Analyzer						
rotameter/valve					CLEAN	
charcoal/mole sieve					REPLACE	
fan					CLEAN	
Teflon filter		REPLACE				
Nephelometer						
optics				CLEAN		
lamp		REPLACE				
Data System						
tape drive/head		CLEAN				
fan filter		CLEAN				
Precipitation Sampler	RINSE					
PAN GC System						
sample inlet		CLEAN				
EC detector					RADIOACTIVE SWAP TEST	

devices were calibrated and made traceable to NBS standards. The dry test meters for establishing flows of the dichotomous samplers were calibrated and certified by EMSL/QAD prior to being put into service in the field.

Quality control between calibrations consists of visual inspection by the operator, who notes any abnormalities while the samplers are in operation and checks the chart record kept for each monitor. The loss of any data as indicated by this record is identified, documented, and corrected. EPA's Type 3B Data Form provides quality control of the aerosol samples taken by the dichotomous sampler. Any variation in duration of a sample run, variation of normal (16.7 liters/min) flow rate, or other problem is entered on this form. Additionally, the first pair of filters is not used for sampling and is kept as a background blank to which the other filters are referenced. Samples and their respective data forms are reviewed by MTL program management personnel and any necessary steps are taken.

Quality control for the high-volume samplers began by certifying the calibration devices at EMSL/QAD to assure the accurate flow references of the orifice. Once each hi-vol system is calibrated and its flow controller set at a Dixon chart reading corresponding to a 50 ft^3/min flow, the field operator monitors the Dixon reading during subsequent sampling. Should this vary by more than 5% of the desired flow, an adjustment to the set flow is made.

All flows, sample duration times, and atmospheric conditions are documented on standardized filter folders. Field personnel examine the hi-vol filters to

check for air loss around the face plate gaskets. Field personnel also note any unusual local environmental condition (burning or plowing of fields, etc.) and any abnormalities such as impaction of insects or holes that may affect a sample's validity. A recalibration of the samples occurs after every 20 samples to insure that consistent sampler characteristics are met. Off-site program management review hi-vol samples as they are received from the field for validation, physical damage, sample durations, and validity of flows as recorded upon the Dixon chart.

Off-site personnel also perform presample and postsample weighing. Prior to weighing, all filters are stored in a desiccator for 24 h to minimize errors due to absorption of water. Each filter is weighed individually on an analytical balance (with accuracy to 0.1 mg) to obtain the presample weight. Lots of clean filters are subdivided into groups of 100. Of each group of 100, 7 are reweighed to verify the precision of measurements. A difference of more than 2.8 mg for any one of the 7 results in a reweighing of all filters in that lot. These weights are documented in a laboratory log and on the individual filter jackets used to contain the filters for field shipment.

When filters are received at the laboratory, they are arranged in somewhat smaller lots and again stored in a desiccator for 24 h to condition the sampled filters to their original state. Each filter is reweighed on the same or a comparable analytical balance. If a large, abnormal deposit (e.g., insects) is found on a sample, it is removed and the sample validity determined. There is an examination for any materials dislodged from the filter during shipment and attempts are made to return these substances to the filter sample

prior to reweighing. Four filters out of each lot are randomly selected for reweighing. If any reweighed sample differs by more than ±5.0 mg, all the filter samples in that lot are reweighed. These reweighings are documented on the individual filter jacket and on the laboratory log. Filters and copies of the laboratory logs are archived for future reference and retrieval. All notes and observations having to do with sampling or measurement abnormalities accompany the documentation of each sample set.

In addition to the calibrations of the gas analyzers every 3 days, these instruments also receive daily zero and span checks. After completion of this routine, the site operator determines whether the instrument tests indicate a need for maintenance, repair or special recalibration. Test atmospheres are generated using an on-site dynamic calibration system that carries or mixes all gases in components made only from Teflon or glass. Flows are maintained with the use of mass flow controllers. These flows are then measured using bubble flowmeters calibrated and traceable to NBS standards, corrected to standard temperature and pressure. These flows and concentrations are recorded on standardized forms and are entered on strip charts. Calibration NO and SO_2 gases are either certified by EMSL/QAD or are assayed in the field using certified NBS or EMSL/QAD standards to establish concentration. These gases and the zero air (containing 350 ppm CO_2) are contained in aluminum cylinders with stainless steel regulators and are stored indoors to maintain concentration stability and mixture homogeneity.

The O_3 generator used in zero spans and calibrations at each site is referenced to a calibrated Dasibi Transfer Standard every 60 days to insure

the stability of the UV light used to irradiate the air and to produce O_3. The Dasibi Transfer Standard is referenced by a certified photometer semi-annually as a quality control measure to maintain the reliability of the transfer standard and thus of the O_3 generation source at each site.

Visual inspection, electronic checks of instrument test points, and pneumatic leak checks complete the routine quality control of the gas analyzers. Any questionable condition is addressed by the site operator and is noted in the site's standard documentation.

Quality control of the meteorological equipment is accomplished by visual checks of the soundness of the system's operation and reasonableness of instrument responses. Every third day the dew point and temperature are measured using a sling psychrometer and compared to the responses of the appropriate instrumentation through the data acquisition system. These measurements are recorded on a standard form and kept by the ORV program manager for future use. Should an error in excess of 10% be detected, the cause is immediately determined and steps are taken to improve these measurements.

Quality control samples for precipitation are prepared off-site every 60 days and are shipped to each monitoring site under refrigeration to preserve sample integrity. These samples contain three different pH levels and three different concentrations of ammonium, sulfate, and nitrate ion. Each site includes a quality control sample with each batch shipment submitted for analysis. This sample is identical in appearance to the other samples, but is

identified to the ORV program manager by the site operator so that an evaluation of the laboratory's analyses can be made.

The data acquisition systems are monitored on a daily basis. A daily check is made of the strip chart recorders monitoring the SO_2, O_3, NO, NO_2, and nephelometer responses. The accuracy of those responses is checked during the zero-and-spans of these systems and agreement between the strip charts, desk-top computer, and panel meters is verified. The strip chart is marked daily as a time check and zeroed by shorting the inputs. Additionally, any nonvalid data captured overnight or during zero spans, calibration, audits, or maintenance are identified on the strip charts.

The ORV program manager periodically reviews the charts received from the field and compares these for data reasonableness and for completeness of daily operations performed on the instrumentation. He also compares, on a spot basis, agreement of data recorded on the strip charts and data generated from the data tapes of the desk-top computer. The inspection of the strip charts may also reveal maintenance or site system failures that escaped the on-site operators.

Data Handling

The Hewlett-Packard 9825 desk-top computer system acquires data from all analog channels once per minute and computes the hourly average for each

pollutant. Each analog channel is compressed into a single number such that the first two digits of the number represent the number of scans and the last three digits represent the hourly average. The software includes the capability of handling wind information using trigometric averages. The software also includes a mechanism for deleting data obtained during calibration.

The field data tapes accumulate 30 days of data and are retrieved by MTL at monthly intervals for transcribing. (Initially, the tapes were retrieved every 2 weeks until operational history was gained.) MTL originally planned to use a Hewlett-Packard 21 MX-E Computer System for the data processing functions necessary to provide EPA with an edited or corrected data tape. However, due to management's decision to replace the Hewlett-Packard computer, a Data General computer is used to process the data. From an edited nine-track data tape, MTL prepares (1) averages calculated for different averaging time periods, (2) frequency distributions for specified parameters, (3) diurnal averages plotted for selected time periods, and (4) summary of calibration data.

The nine-track magnetic tape is used to generate a printout on which the raw data are converted to physical units. The transfer equation programs perform this task. There are several alternatives that may be used in converting the voltages into physical units. Based on calibration procedures and goals of the study, linear regression analysis is applied to the calibration data for the data pairs at the 3-day calibration interval. The general form of the transfer equation is: concentration (ppm) = $M(V + V_o)$, where V is the analyzer output voltage and M is the calibration constant.

For wind direction, the software of the data system computes hourly averages using trigometric techniques. The vector averaging for wind speed and direction is also used in the data processing to obtain calculations for longer periods. Similar transfer equations are used for the other meteorological equipment to convert sensor voltages to data in appropriate physical units.

Validation screening procedures include: searches for large negative values of pollutant concentration, excessively large hourly averages above a preset maximum limit, comparisons to strip chart readings, and reviews of calibration and span drift data. A further validation procedure is a random check of strip chart data against the archived data. On every third day during calibration of the analyzers, an additional validity check is performed using in-station span values. Small tolerances are permitted in each of the validation checks. Since some values are obtained from the strip charts by visual inspection, some differences in the values can be expected. If the difference exceeds the preset tolerances, an error is noted.

ACTIVITIES NEAR THE STATIONS

The operators made the following observations about local activities which may affect the measurements.

West Station

The station is in a pasture; the nearest agriculture field is at 130 m and 0°. The next nearest field is at 0.5 km and 205°. Corn is the principal

crop. The dry fertilizer most used in the area is 0% nitrogen, 40% phosphate, and 60% potash, with anhydrous ammonia also used for corn.

Only a few isolated incidents of burning in fields occur, but the operator can occasionally smell smoke from residential wood burning. The nearest house is at 150 m and 300°.

Center Station

Agricultural plowing occurs SE and E of the station. Planting occurs during May and the end of April; herbicides are used but their effects are not observed on the gas monitors. Fertilizers are mostly used in liquid form. On May 15 and 16, 1980, use of pesticides, herbicides, and fertilizers and tilling occurred near the station.

Burning in agricultural fields is very limited. The operator observed such an event only once, on May 16, 1980, from 1300 to 1800; this event brought smoke into the station itself. Residential wood burning is common in the area, but the operator has never smelled smoke.

The passage of tractors and school buses causes a brief NO spike but no evident effect on the hourly averages.

A company which produces roofing materials of asphalt impregnated paper and tar impregnated fiberglass is located at about 7 km. The odor is noticeable at the station when the wind is S to SE during the heating. The only instrument

response observed is on the sulfur monitor, where readings can exceed 100 ppb; the event usually lasts 1 to 2 h.

The operator has noticed that around 0600 with a S to SE wind, he can often see a brown haze to the S and blue sky to the NW. If the wind persists for several hours, brown haze is observed at all points on the horizon and all monitors show elevated, but not off-scale, readings. He believes that Cincinnati is the source of the brown haze.

During November 13 and 14, 1980, forest fires occurred in eastern Kentucky. Nephelometer, SO_2, and NO_x readings were high; the operator smelled smoke and attributes a sore throat to high pollution levels.

East Station

The station is on private property but is surrounded by state forest and is buffered from direct contact with farmland (the principal land use in that region). The nearest farm is 1 mi W of the station. Most plowing occurs in the spring; fertilizers and herbicides are used.

From May 1980 to June 1981 only three area farmers reported the burning of fields to the state forest fire warden. Two fires were in March 1981: ½ acre was burned E of the station and 1 acre was burned W. The third was a burn of 9 acres to the N in April 1981. No fields were burned within 8 km of the station. Residential wood burning and camp fires may affect the site; occasionally the operator has smelled smoke. Nearly every weekend during the

summer, lawn mowers are operated near the station for several hours. Weekend and holiday traffic to the nearby park is heavy during the warmer months. The Kentucky forest fire of November 13 and 14, 1980 was observed at the station: SO_2, NO_x, and nephelometer readings increased and the operator smelled smoke.

SECTION 4

RESULTS AND DISCUSSION

As mentioned in Section 1, this section presents only some aspects of the data and does not provide a complete analysis. This section is divided into subsections according to the length of interval surveyed. In the first subsection, mean values are presented for the entire sampling period: May to December 1980. These numbers permit a general comparison of the three sites and will be compared in future reports with long-term averages to test for trends.

The second section presents monthly means and includes indications of the percent of data recovered. We also report whether these monthly averages are dominated by brief episodes. This discussion will explore the importance of events in contributing to the average values; for example, in comparing the averages for the entire data period, one should note whether the values from a given site are dominated by values during one particular month. Likewise, in comparing monthly averages, one should determine whether episodes of a few days determine the monthly average. Brief reports are included on aerosol carbon, sulfur distribution between gases and particles, sulfur speciation, and compound analysis of aerosols. We also present information on two brief events: the aerosol chlorine event and the forest fire.

AVERAGES FOR THE PERIOD MAY TO DECEMBER 1980

The mean atmospheric concentrations for aerosols and gases and the mean scattering coefficients are presented in Table 4-1. The fine aerosol masses for the three sites all lie within 10% of their mean. The fine aerosol sulfur, if present as ammonium sulfate, accounts for 50% to 55% of the fine mass at all three sites. Sulfur is the most abundant measured element in the fine aerosol fraction; this is consistent with most aerosol analyses, but elements lighter than aluminum are not detected and oxygen or carbon, for example, may contribute the greatest amount of mass. The next most important fine aerosol element in cities is usually lead; however, the lead contribution to aerosol mass at the ORV sites is only about 0.2% to 0.3%. This low lead concentration indicates that automobile traffic is only a minor contributor to the aerosol. After sulfur, the most abundant fine aerosol elements are silicon and potassium. In urban areas, the elements of greatest importance after sulfur are often bromine, iron, and zinc, but these elements are present at mean levels below those of silicon and potassium at the ORV sites.

The coarse aerosol masses and composition are typical of materials in the Earth's crust. The higher levels at the West and Center stations are due, we believe, to the location of these sites on or near agricultural fields and the location of the East station in a state forest.

Aerosol coarse, fine, and total masses are shown in Figures 4-1, 4-2, and 4-3. Zero values occur when the dichotomous samplers did not operate. Tick marks on the x axis coincide with Sundays. The figures show that the dominance

TABLE 4-1. MEAN VALUES FOR GASES, SCATTERING COEFFICIENT, AND AEROSOL COMPOSITION

Variable	Station		
	West	Center	East
Gases (ppb)			
NO	2.1	2.5	3.8[a]
NO_2	6.3	8.4	8.3
O_3	39	35	35
SO_2	7.7	8.3	6.9
b_{scat} (10^{-4} m^{-1})	1.9	1.9	1.3
Aerosol Composition ($\mu g/m^3$)[b]			
Mass - F	21.5	21.8	18.6
Mass - C	13.0	10.8	7.2
S - F	2.72	2.91	2.41
S - C	0.19	0.18	0.17
Pb - F	0.05	0.06	0.06
Pb - C	0.009	0.01	0.01
Si - F	0.16	0.11	0.07
Si - C	1.88	1.55	0.87
Al - F	0.06	0.07	0.02
Al - C	0.60	0.53	0.29
Ca - F	0.07	0.06	0.03
Ca - C	0.73	0.64	0.29
Fe - F	0.07	0.08	0.06
Fe - C	0.34	0.27	0.21
K - F	0.12	0.08	0.07
K - C	0.17	0.14	0.09

[a]Dominated by the July 11-15 event.

[b]Legend: F, fine; C, coarse.

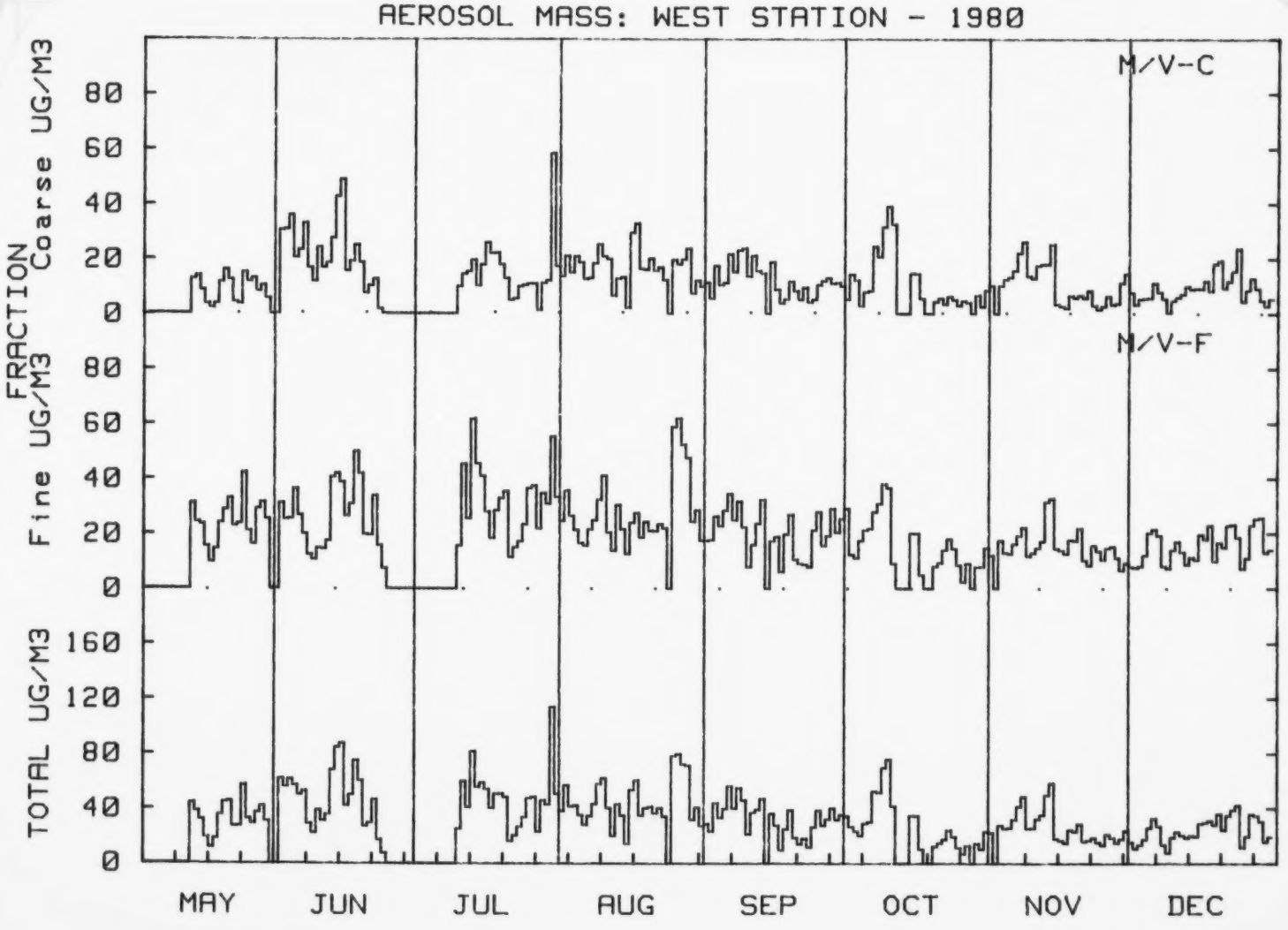

Figure 4-1. Aerosol coarse, fine, and total mass at West station.

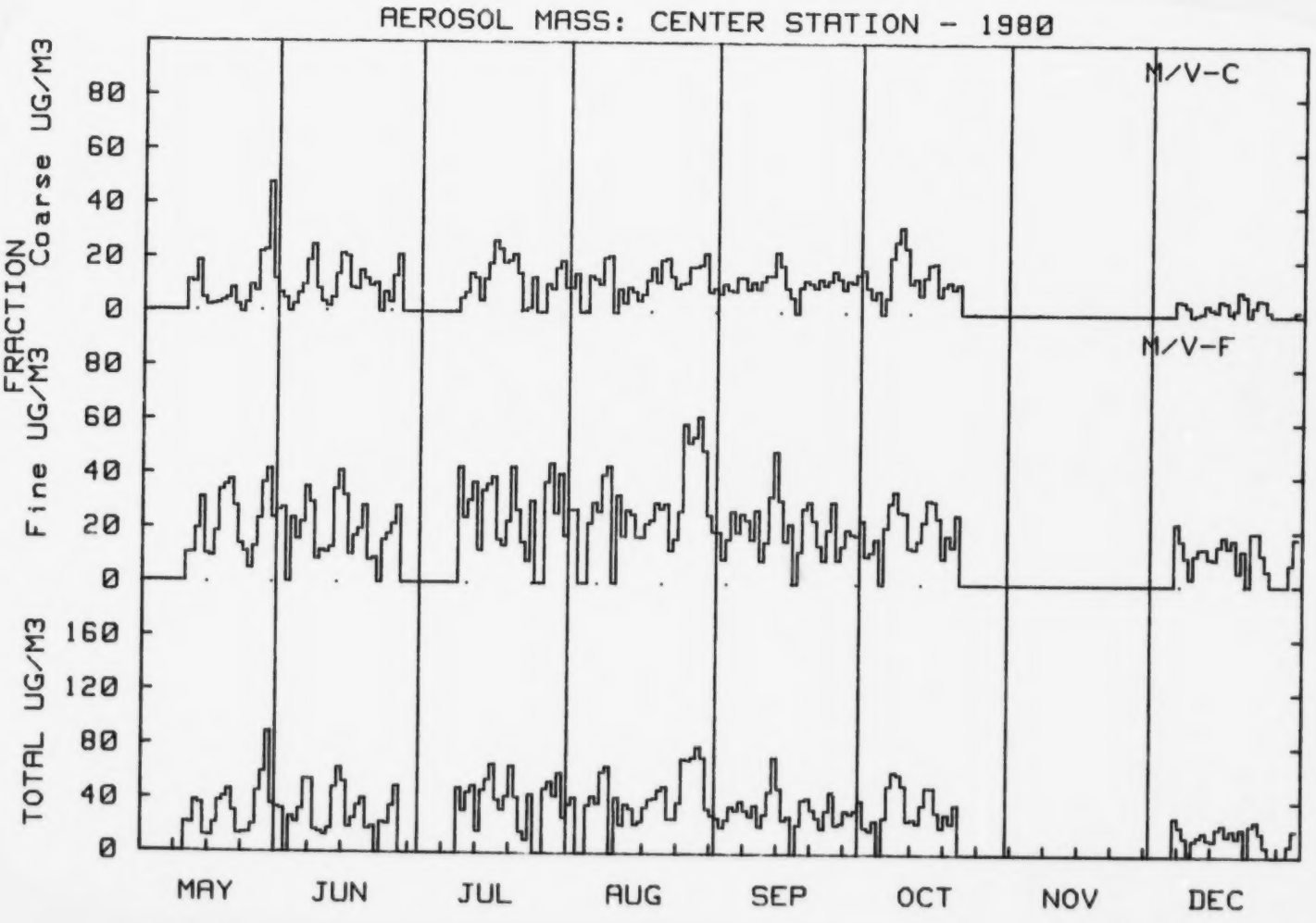

Figure 4-2. Aerosol coarse, fine, and total mass at Center station.

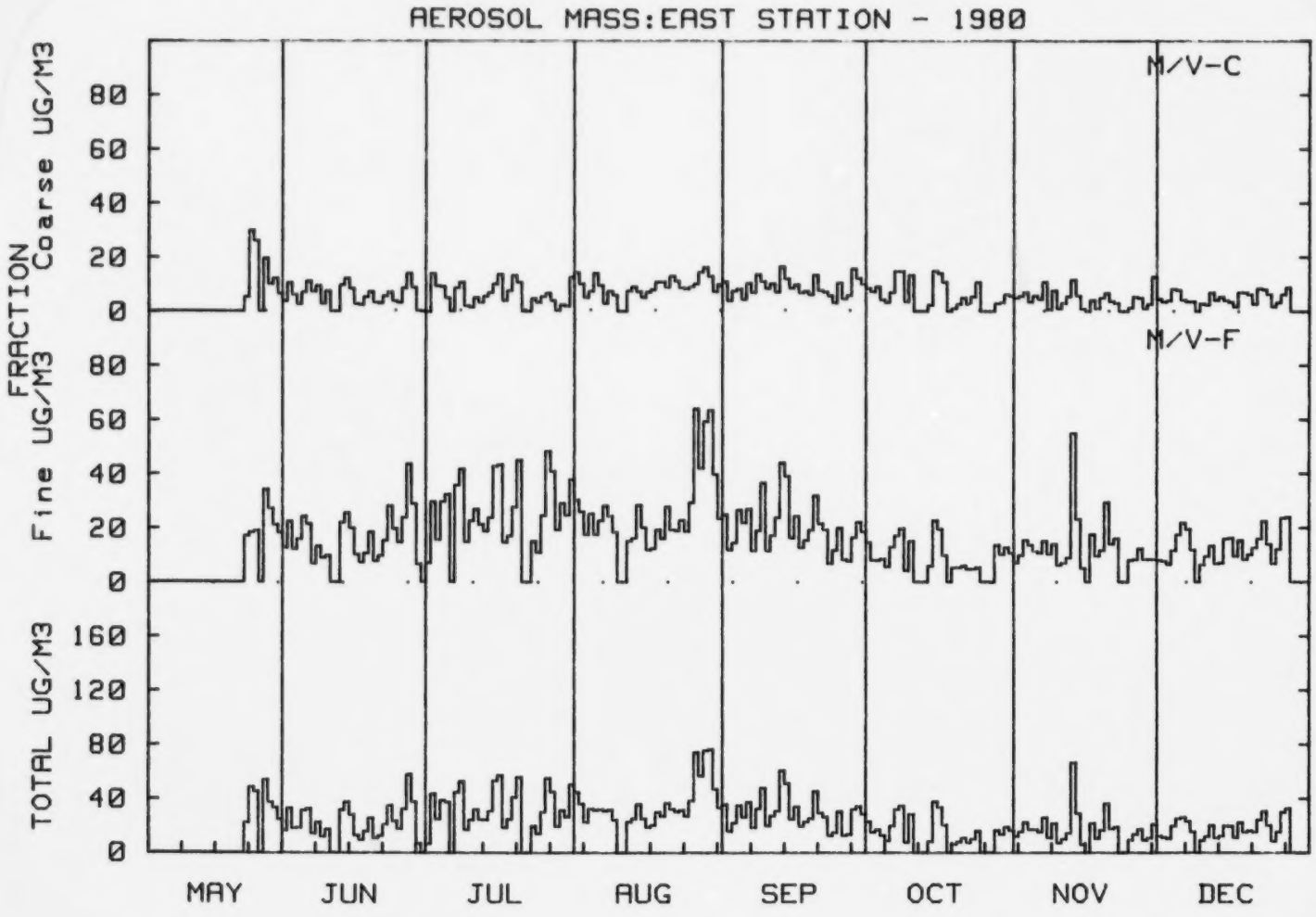

Figure 4-3. Aerosol coarse, fine, and total mass at East station.

of fine over coarse aerosol mass is systematic and not due to occasional events. Events which occurred at more than one station are evident; for example, an increase in fine mass at the end of August. There is also an indication of the mid-November forest fire (mentioned in the previous section) at the West and East stations; unfortunately, the sampler at the Center station was inoperative during November.

Single Site Correlation Coefficients

The correlation coefficient R(x,y) is defined as Co Var(x,y)/(Var(x)Var(y))$^{\frac{1}{2}}$ and indicates whether x and y are correlated to some arbitrary level of confidence. The numbers of valid aerosol samples collected during the period May to December 1980 were 344, 303, and 328 at the West, Center, and East stations, respectively; the values of the correlation coefficient for data sets of this size at significance levels of 95% and 99.9%, respectively, are 0.11 and 0.17.

Correlation coefficients for aerosol masses and most abundant elements are given in Table 4-2. It is evident that a high degree of correlation exists between sulfur and aerosol mass and between lead and bromine in the fine fraction and among aerosol mass and the crustal elements aluminum, silicon, iron, and calcium in the coarse fraction.

The slopes and intercepts formed by linear regression using least squares are given in Table 4-3. To interpret these values, consider a hypothetical case in which the fine aerosol fraction is composed entirely of $(NH_4)_2SO_4$;

TABLE 4-2. CORRELATION COEFFICIENTS FOR AEROSOL MASS AND COMPOSITION

Correlated Variables[a]	Station		
	West	Center	East
Mass - F vs. Mass - C	0.43	0.45	0.46
Mass - C vs. Al - C	0.50	0.78	0.68
Si - C vs. Al - C	0.95	0.80	0.91
Si - C vs. Fe - C	0.96	0.88	0.87
Si - C vs. Ca - C	0.66	0.67	0.82
Si - C vs. K - C	0.95	0.92	0.94
Mass - F vs. S - F	0.87	0.92	0.93
Br - F vs. Pb - F	0.78	0.85	0.80

[a]Legend: F, fine; C, coarse.

TABLE 4-3. SLOPE AND INTERCEPT FROM LINEAR REGRESSIONS AMONG AEROSOL MASSES AND COMPOSITIONS

Regression Pair[a]	Station					
	West		Center		East	
	Slope	Intercept	Slope	Intercept	Slope	Intercept
Mass - F vs. S - F	4.9	8 μg	5.2	7	5.3	6
Br - F vs. Pb - F	0.14	2 μg	0.12	2	0.15	0.8
Mass - C vs. Al - C	15	4 μg				
Si - C vs. Al - C	2.9	140 ng				
Si vs. Fe - C	6.5	-280 ng				
$(NH_4)_2SO_4$ vs. S	4.1	0				
Crustal Shale						
Mass vs. Al	12.5	0				
Si vs. Al	3.4	0				
Si vs. Fe	5.8	0				

[a]Legend: F, fine; C, coarse.

the slope and intercept of the regression Mass-F vs. S-F would then be 4.1 and 0, respectively. The observed values of 4.9 to 5.3 and 8 to 6 μg suggest that, of the fine mass, 6 to 8 μg do not vary with sulfur abundance. The remaining mass, which does vary with sulfur abundance, is 4.9 to 5.3 times that of sulfur. Since the mass ratio of $(NH_4)_2SO_4$ to sulfur is 4.1, and assuming that all fine sulfur is present as $(NH_4)_2SO_4$, we may infer that conditions conducive to the passage of sulfur into the sampling areas (meteorology, sources etc.) also bring in other materials amounting to a mass of about 20% that of the $(NH_4)_2SO_4$.

Applying similar interpretations to the results of linear regression among the coarse mass and elements, we find that 4 μg of coarse mass do not vary with aluminum. The relative values of aluminum, silicon, and iron are consistent with crustal shale values used by Dzubay[15] in his chemical element balance calculations for St. Louis aerosol data.

Ratios of mean abundances of crustal elements are given in Table 4-4 along with crustal shale ratios. The agreement of the observed values in the coarse aerosol fraction with shale values is quite close, except for calcium. If we include crustal limestone in our comparison, the calcium values would also be brought into close agreement. The observed ratios in the fine aerosol show an increase of a factor of 2 to 4 in relative iron values and of about 10 in relative potassium values.

The agreement shown in Table 4-4 between element ratios for aluminum, silicon, calcium, iron, and potassium in the coarse aerosol and in crustal

TABLE 4-4. RATIOS OF MEAN ELEMENTAL ABUNDANCES

Source of Data	Ratio			
	Al/Si	Ca/Si	Fe/Si	K/Si
Crustal Shale	0.29	0.08	0.17	0.10
Coarse Aerosol				
West station	0.32	0.39	0.18	0.09
Center station	0.34	0.41	0.17	0.09
East station	0.33	0.33	0.24	0.10
Fine Aerosol				
West station	0.38	0.44	0.44	0.75
Center station	0.64	0.55	0.73	0.73
East station	0.43	0.43	0.86	1.0

shale and limestone suggests that suspended soil is the source of these elements in coarse aerosols. The high correlation coefficients among these elements in Table 4-2 also suggest dominant contributions of these elements from one source.

Observations of the same element in both the coarse and fine aerosol fractions raise the question of whether or not both fractions share a common source for that element. The problem may be complicated if different sources emit elements in similar abundance ratios. The coarse aerosol fraction often consists of suspended soil in which silicon and aluminum are the most abundant elements (neglecting oxygen) and the observation of silicon and aluminum in the fine aerosol fraction may also be due to suspended soil. Fly ash particles, however, are also most abundant in silicon and aluminum (neglecting oxygen). If a given element that is found in both aerosol fractions is from one source,

one would expect a high correlation coefficient for the elemental abundances in both fractions. A high correlation coefficient is not evidence for one source because the time variation may be dominated by meteorology so that different sources not correlated in emissions may contribute particles that arrive in a correlated manner at the aerosol sampler. In the case investigated here, it may seem unlikely that weather patterns induce observed correlations between the amount of suspended soil and the amount of fly ash emitted from power plants. One may imagine, however, circumstances in which high wind speeds would be associated with increased power demand. If, on the other hand, the observed correlation coefficient is zero, then one may say with confidence that different sources contribute to the fine and coarse aerosol fractions unless the pattern of dispersal of the two elements is sufficiently different so that a significant correlation present at the source is diminished during transport to the sample collector.

The foregoing discussion assumes that the experimental errors are small with respect to the elemental amounts measured because random errors reduce the correlation coefficient. The correlation coefficient (ρ) depends on the experimental uncertainties, as:

$$\rho = \frac{\text{CoVar}\ (X,Y)}{(\text{Var}\ X + \overline{\varepsilon^2})^{\frac{1}{2}}(\text{Var}\ Y + \overline{\vartheta^2})^{\frac{1}{2}}}$$

where ε and ϑ are the experimental measurement errors in X and Y, respectively. We have examined the data discussed in this section and determined that

experimental errors in elemental analysis do not significantly affect the correlation coefficients as we have used them.

The first group of correlation coefficients in Table 4-5 shows significant correlations between the fine and coarse fraction abundances of a number of elements. These correlations are not so large as those for different elements within the same fraction (Table 4-2). These results suggest that different or additional sources contribute these elements in the fine fraction.

The second group of coefficients in Table 4-5 show significant correlations for silicon with calcium, aluminum, and iron in the fine fraction but a much reduced correlation with sulfur. These results suggest that at least one common source exists for aluminum, silicon, calcium, and iron in the fine fraction. That source either does not contribute sulfur or contributes it in a form for which the dispersal pattern is sufficiently different from the other elements to obscure the source correlation.

The last two groups of correlation coefficients in Table 4-4 are those for various elemental fractions and potassium, which has been observed in relatively high concentrations in plumes from combustion of vegetative material and fossil fuel. The rather high correlations in the coarse fraction along with the close agreement of the observed and crustal shale K/Si ratio in the coarse fraction suggest that the coarse potassium comes mostly from suspended soil. The reduced correlation coefficients for potassium with other elements in the fine fraction suggest more complex sources than in the coarse fraction. As Table 4-4 shows, the K/Si ratio is considerably elevated with respect to

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crustal shale in the fine fraction, and the Fe/Si ratio is markedly elevated. Because potassium is most strongly correlated with iron (Table 4-5), it seems possible that these elements have a common source.

TABLE 4-5. CORRELATION COEFFICIENTS FOR ELEMENTS IN THE FINE AND COARSE AEROSOL FRACTIONS

Correlated Variables[a]	Station		
	West	Center	East
Al - F vs. Al - C	0.57	0.56	0.21
Si - F vs. Si - C	0.52	0.50	0.46
Fe - F vs. Fe - C	0.64	0.59	0.61
K - F vs. K - C	0.52	0.38	0.42
Ca - F vs. Ca - C	0.36	0.58	0.63
S - F vs. S - C	0.71	0.38	0.66
Si - F vs. Ca - F	0.72	0.51	0.69
Si - F vs. Al - F	0.90	0.48	0.46
Si - F vs. Fe - F	0.96	0.76	0.54
Si - F vs. S - F	0.03	0.31	0.19
K - C vs. Ca - C	0.70	0.76	0.79
K - C vs. Al - C	0.92	0.79	0.89
K - C vs. Si - C	0.95	0.92	0.94
K - C vs. Fe - C	0.95	0.89	0.84
K - F vs. Mass - F	0.24	0.36	0.31
K - F vs. S - F	0.04	0.23	0.19
K - F vs. Fe - F	0.31	0.47	0.55
K - F vs. Al - F	0.25	0.12	0.05
K - F vs. Si - F	0.32	0.50	0.35

[a]Legend: F, fine; C, coarse.

Multiple Site Correlation Coefficients

In order to determine whether the time dependences of aerosol properties are similar from site to site, we computed the correlation coefficients for

masses and several of the more abundant elements. This was accomplished by accumulating all 12-h runs into 24-h runs. These correlation coefficients appear in Table-4-6.

TABLE 4-6. CORRELATION COEFFICIENTS FOR AEROSOL MASS AND COMPOSITION AMONG THE THREE SITES

Correlated Variables[a]		Fine Fraction	Coarse Fraction
Mass	W vs. C	0.60	0.39
	C vs. E	0.67	0.33
	W vs. E	0.55	0.22
S	W vs. C	0.67	0.25
	C vs. E	0.71	0.16
	W vs. E	0.53	0.34
Si	W vs. C	0.61	0.63
	C vs. E	0.57	0.40
	W vs. E	0.43	0.30
Fe	W vs. C	0.55	
	C vs. E	0.41	
	W vs. E	0.19	
K	W vs. C	0.78	
	C vs. E	0.58	
	W vs. E	0.39	
Pb	W vs. C	0.59	
	C vs. E	0.37	
	W vs. E	0.49	

[a]Legend: W, West; C, Center; E, East.

The number of data pairs and the corresponding 95% correlation coefficients are:

Sites	Pairs	$P_{95\%}$
West -- Center	149	.16
Center -- East	138	.17
West -- East	178	.15

The entries in Table 4-6 show that the correlations for fine fraction mass and sulfur are considerably higher than those for the coarse fraction; this pattern is consistent with the much greater atmospheric lifetimes and transport over greater distances of fine particles. The correlation coefficients for silicon, however, are nearly as large in the coarse fraction as in the fine. This phenomenon could be explained by the likelihood that windy conditions in the ORV will cause increased amounts of suspended solid at all three stations and, consequently, cause a time correlation for silicon among the sites. Notice, however, that we have now invoked two very different explanations for the appearance of large correlation coefficients: (1) long-range aerosol transport for fine mass and sulfur, and (2) conditions causing simultaneous increases from local sources at all three stations for coarse silicon. It is clear that, as pointed out in the previous section, correlation coefficients by themselves cannot provide unique explanations and are most useful to check the consistency of explanations based on other information.

The difficulty of distinguishing between long-range pollutant transport and correlated behavior of separated local sources using time correlations is further illustrated by the correlation coefficients for fine lead. In almost all cases, as expected, correlation coefficients between neighbor sites (West

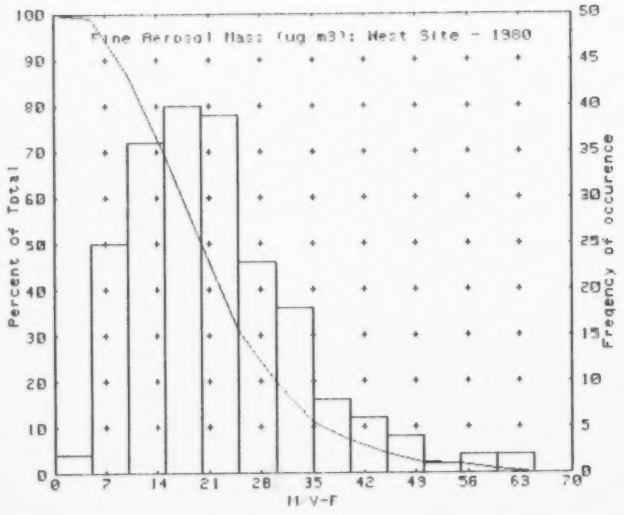
vs. Center and Center vs. East) are larger than those between end sites (West vs. East); the exception is fine aerosol lead. This phenomenon suggests that driving patterns are most similar at the West and East sites.

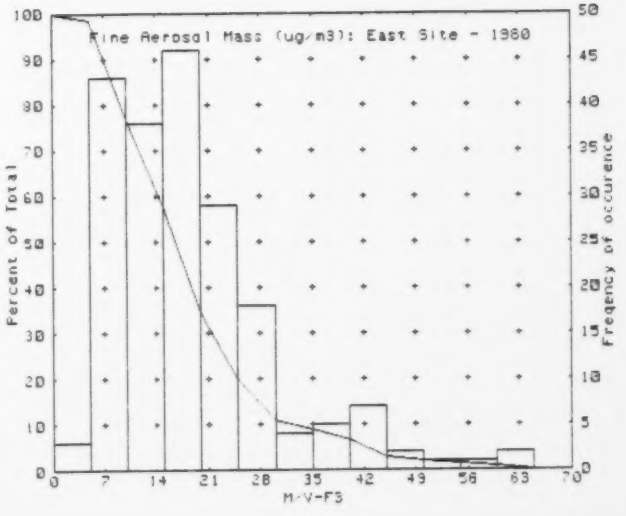
We emphasize that the foregoing discussion of correlation coefficients provides no clear evidence but only suggestive indications for more complete analysis. As we have stated, the magnitude of a correlation coefficient may depend on behavior of sources and on weather patterns.

Frequency Distributions

In order to provide a compact example of available information about the shape of the distribution of atmospheric aerosol concentrations, we computed frequency distributions for fine aerosol mass (Figure 4-4), sulfur (Figure 4-5), and potassium (Figure 4-6) at each of the three sites. The histogram bars show the frequency of occurrence (right ordinate scale) corresponding to values on the abscissa. The smooth curve is the cumulative distribution function; it describes the percent of the population (left ordinate scale) for which the measured value is more than the value on the abscissa.

The frequency distributions for fine aerosol mass and sulfur are approximately the same from site to site. The distribution for fine aerosol potassium shows that events of very high potassium occurred only at the West site.





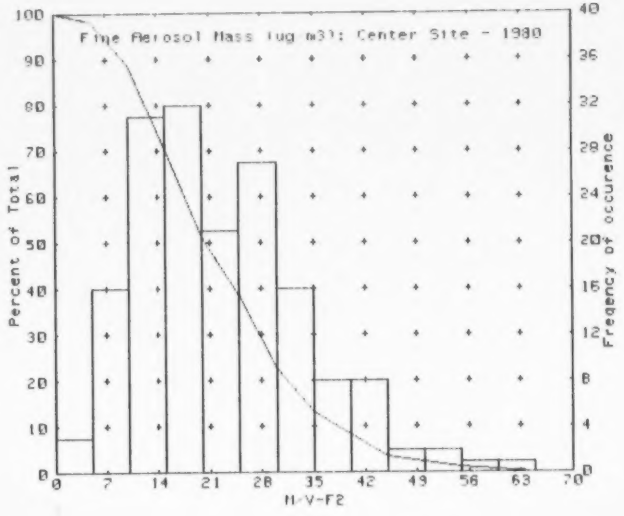


Figure 4-4. Frequency distribution of fine aerosol mass at each station.

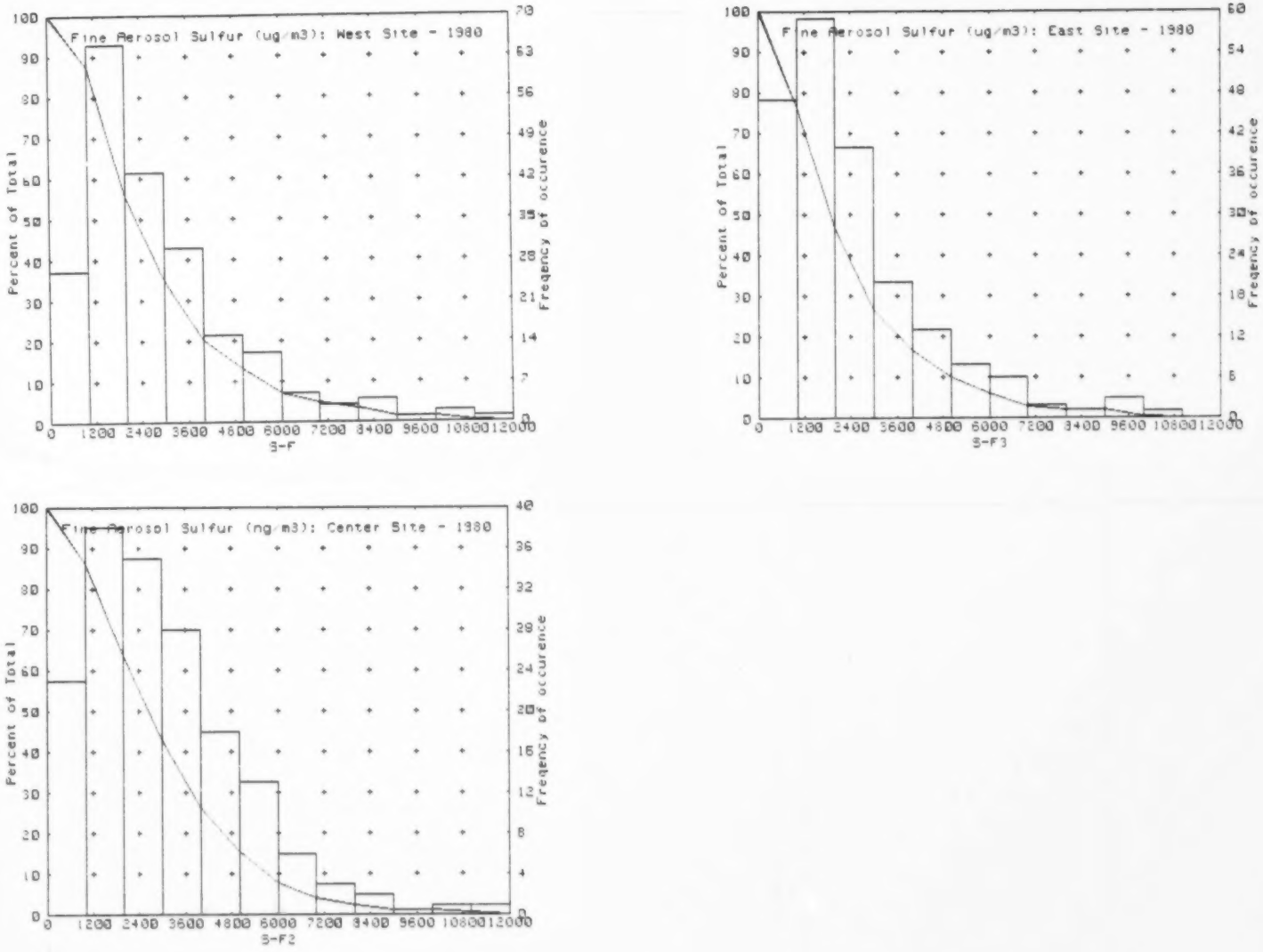
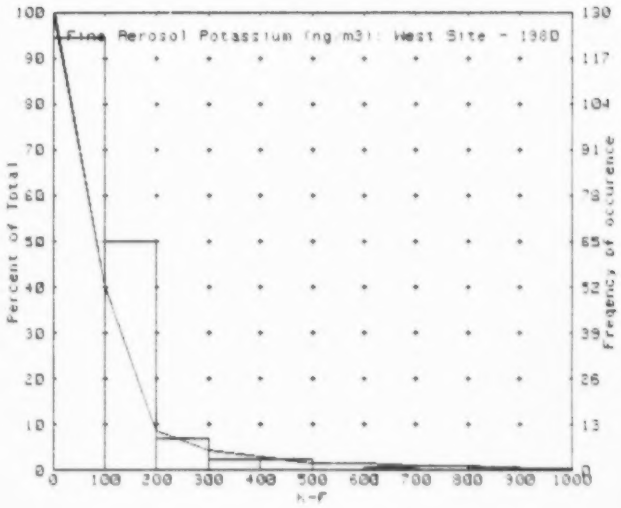
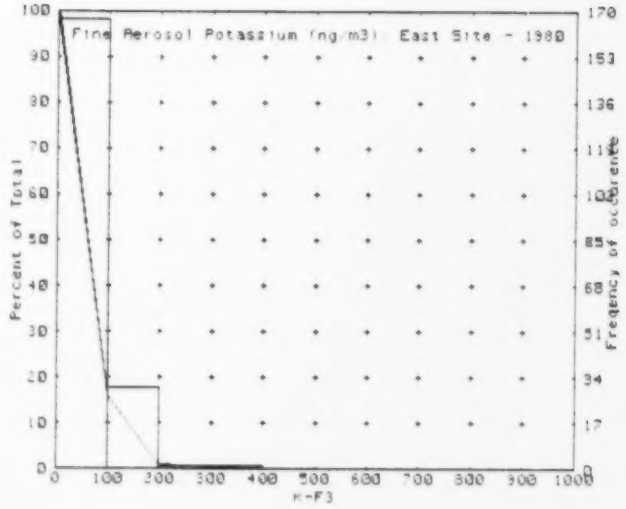


Figure 4-5. Frequency distribution of fine aerosol sulfur at each station.





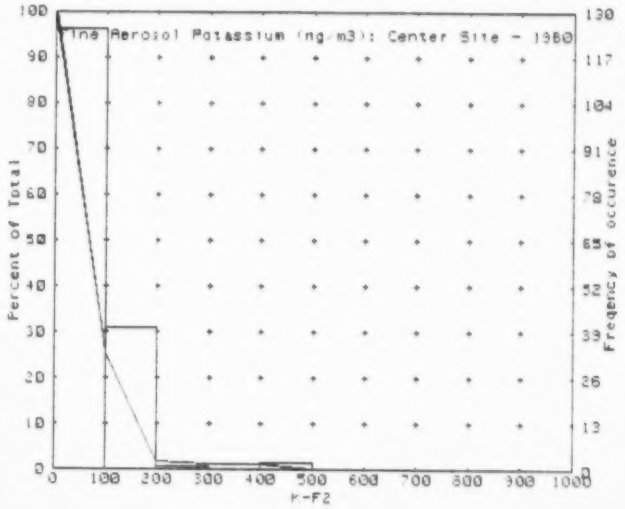


Figure 4-6. Frequency distribution of fine aerosol potassium at each station.

MONTHLY AVERAGES

Monthly average aerosol mass concentrations are shown in Figures 4-7 and 4-8 and Tables 4-7 and 4-8. The fine aerosol mass and sulfur concentrations are systematically lowest at the East site. The West site most often displays the highest mass concentration, and the decrease in fine aerosol sulfur from West to East is marked for most months. This systematic pattern is indicative of conditions in the regions around the three sites and emphasizes the importance of a long-term data base in determining the changes in air quality at a given site. The generally lower coarse aerosol mass values at the East site are most easily explained by its location in a state forest; the other sites are situated in agricultural regions.

Ozone levels are shown in Figures 4-9 and 4-10; these are the maximum (1400 h CST) and minimum (0600 h CST) hourly averages averaged over each month. The maximum averages systematically decrease from west to east.

Nitrogen oxides monthly averages are shown in Figure 4-11 and Table 4-9. The station-to-station patterns are very different from those of the aerosols and ozone discussed above. In general, the NO_x levels are highest at the East site, with an especially dramatic difference in NO during July. This different pattern for NO_x raises the question of the possible effect of short-term events on the monthly average. If the percent of data captured for a given monitor is low for a given period, the average for that period may be biased from the true average. Alternatively, a short-term event of values much

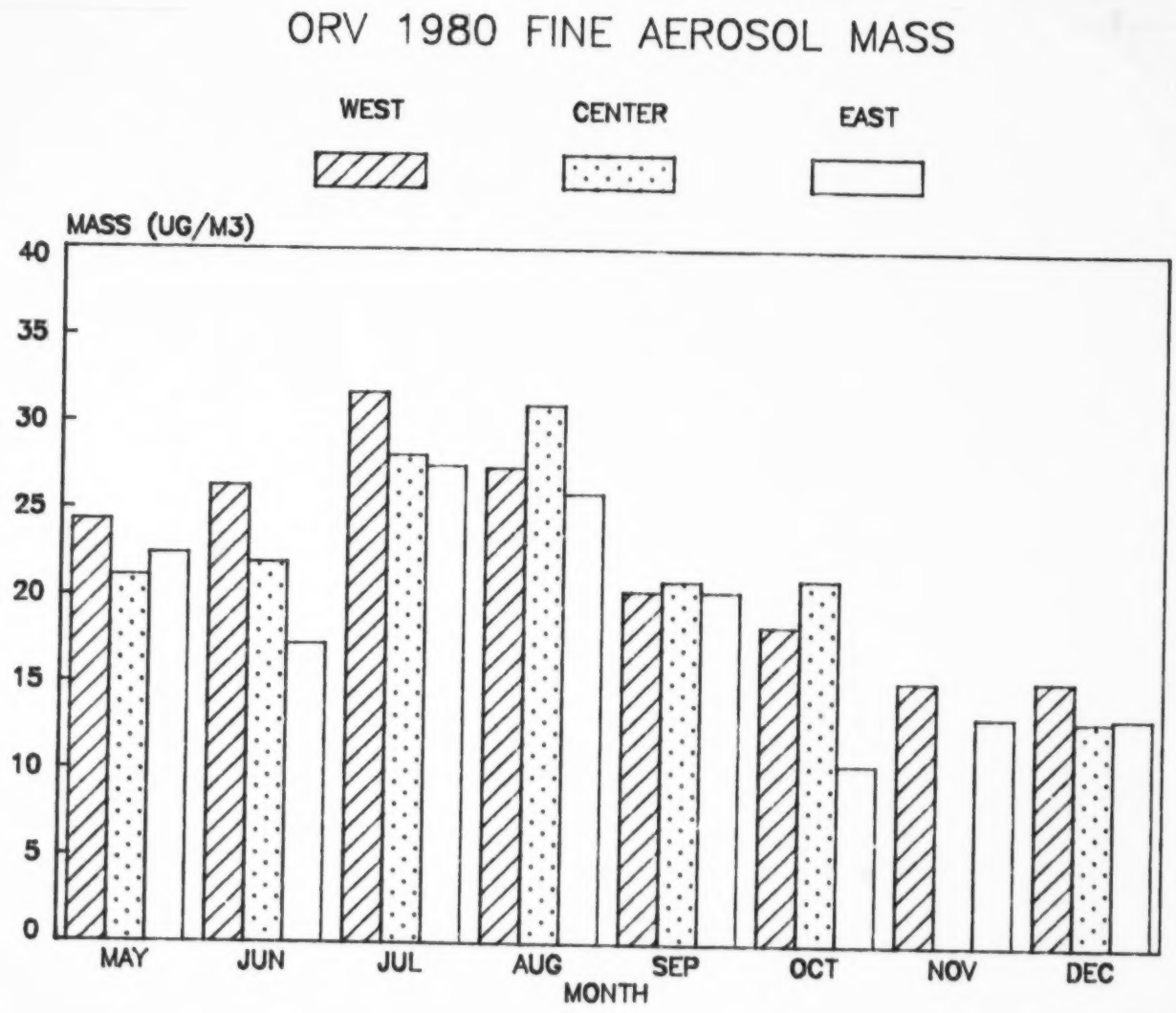


Figure 4-7. Monthly average concentrations of fine aerosol mass at each station.

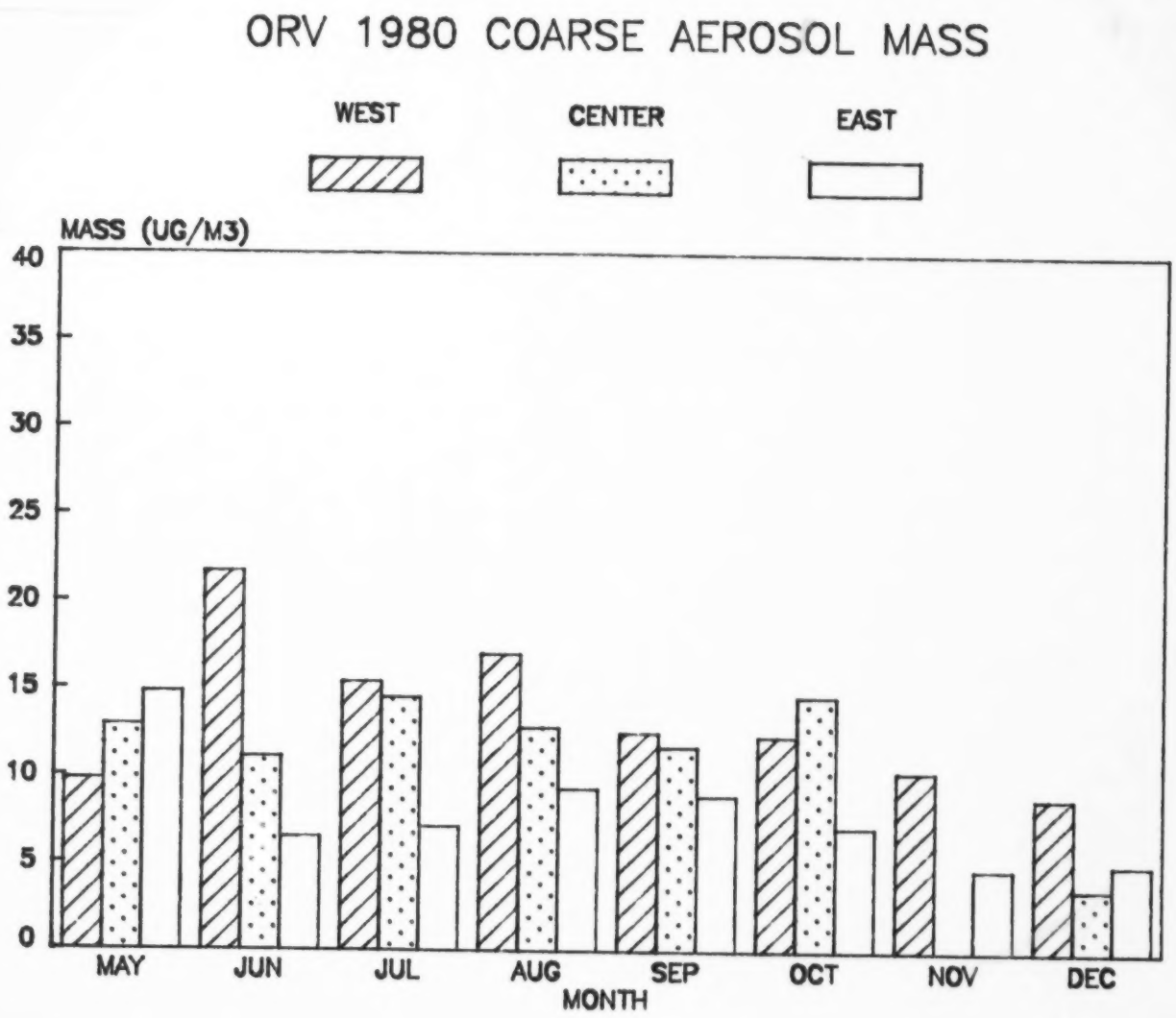


Figure 4-8. Monthly average concentrations of coarse aerosol mass at each station.

TABLE 4-7. MONTHLY AVERAGE CONCENTRATIONS OF ELEMENTS PRESENT IN THE FINE AEROSOL FRACTION AT EACH STATION

Variable[a]		Concentration (x 10^3 $\mu g/m^3$)							
		May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
S	W	4000	3200	4800	3500	3100	1900	1300	1600
	C	3500	2900	4300	4400	2800	1700	-	1600
	E	2900	2200	4000	3900	2500	1400	1100	1400
Si	W	144	122	164	509	100	112	75	74
	C	145	150	109	208	76	102	-	46
	E	100	72	66	119	64	52	40	68
K	W	73	187	87	141	65	143	135	105
	C	91	112	69	85	55	67	-	88
	E	87	57	61	63	51	66	90	92
Fe	W	65	61	69	191	43	56	44	42
	C	107	86	67	101	59	74	-	49
	E	75	47	53	69	49	60	59	56
Pb	W	59	44	51	39	54	54	57	55
	C	69	58	62	60	71	59	-	58
	E	69	46	70	60	62	67	59	30
Mass[b]	W	24.3	26.3	31.7	27.4	20.3	18.3	15.2	15.3
	C	21.1	21.9	28.1	31.0	20.9	21.0	-	13.0
	E	22.4	17.2	27.5	25.9	20.3	10.4	13.2	13.2
%dr	W	52	78	68	94	90	66	100	100
	C	63	72	60	84	95	60		68
	E	21	88	84	87	92	69	100	87

[a]Legend: W, West; C, Center; E, East; %dr, percent data recovered.

[b]In $\mu g/m^3$.

TABLE 4-8. MONTHLY AVERAGE CONCENTRATIONS OF ELEMENTS PRESENT IN THE COARSE AEROSOL FRACTION AT EACH STATION

Variable[a]		Concentration (x 10^3 $\mu g/m^3$)							
		May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Si	W	1410	3350	2720	3030	1454	2015	1489	568
	C	2366	2063	2132	1653	1149	1810	-	589
	E	2069	938	978	819	747	1007	656	709
Ca	W	574	842	1020	794	716	952	787	444
	C	647	765	1083	613	658	786	-	250
	E	530	289	349	204	256	404	300	228
Al	W	453	1030	807	1080	456	609	475	144
	C	498	603	701	570	570	902	-	190
	E	613	255	342	317	288	306	198	255
Fe	W	250	502	454	532	273	327	270	206
	C	349	334	352	305	227	259	-	132
	E	349	203	220	184	197	245	188	212
S	W	388	233	273	232	222	117	122	84
	C	119	91	390	231	166	99	-	203
	E	185	93	223	225	243	153	85	134
K	W	133	254	231	246	165	181	126	95
	C	184	175	200	161	131	157	-	52
	E	187	99	108	99	95	99	59	63
Mass[b]	W	9.8	21.7	15.4	17.0	12.5	12.3	10.3	8.8
	C	12.9	11.1	14.5	12.8	11.7	14.6	-	3.6
	E	14.8	6.5	7.1	9.3	8.9	7.1	4.7	5.0

[a]Legend: W, West; C, Center; E, East.

[b]In $\mu g/m^3$.

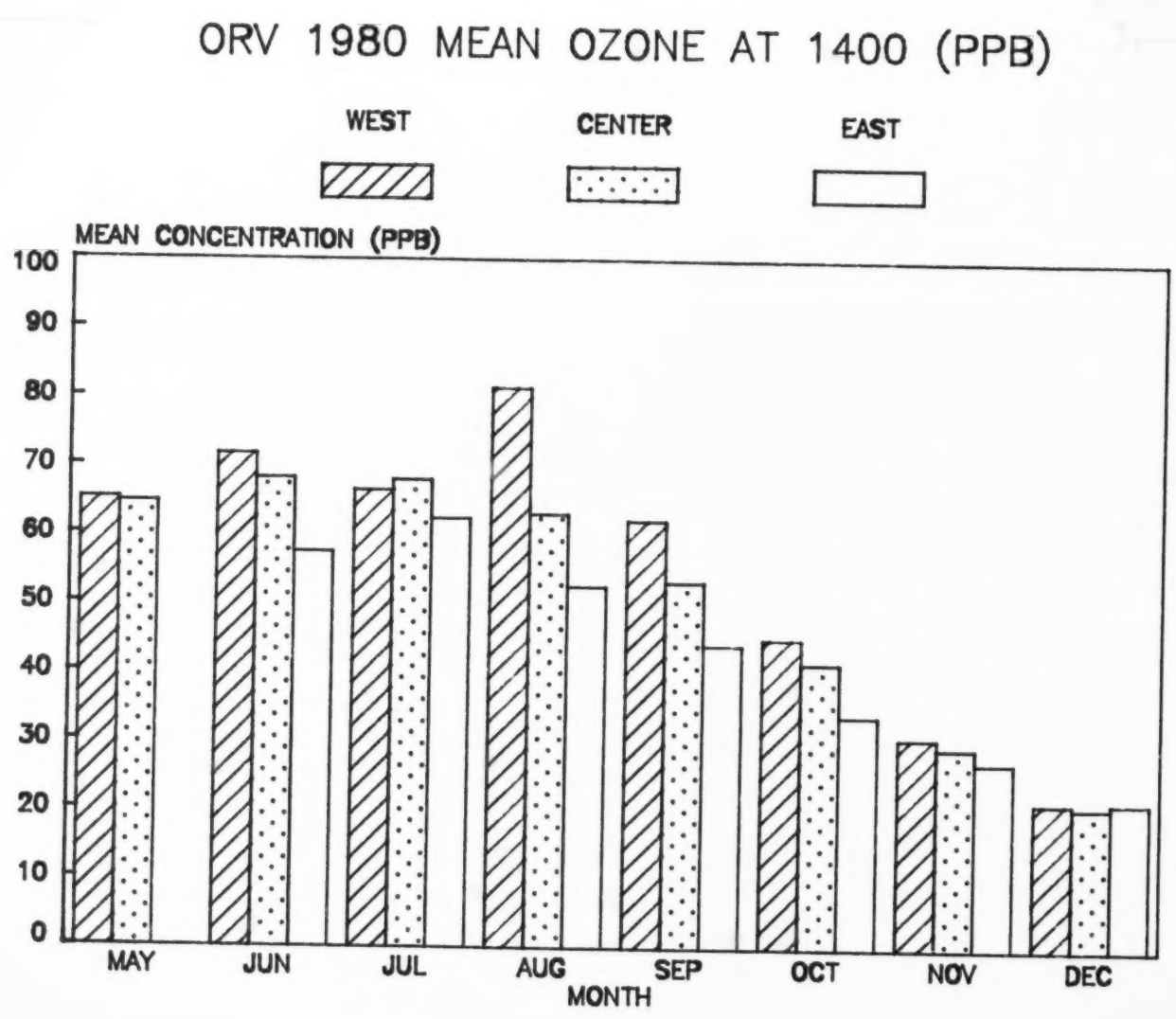


Figure 4-9. Average ozone concentration at 1400 h by month for each station.

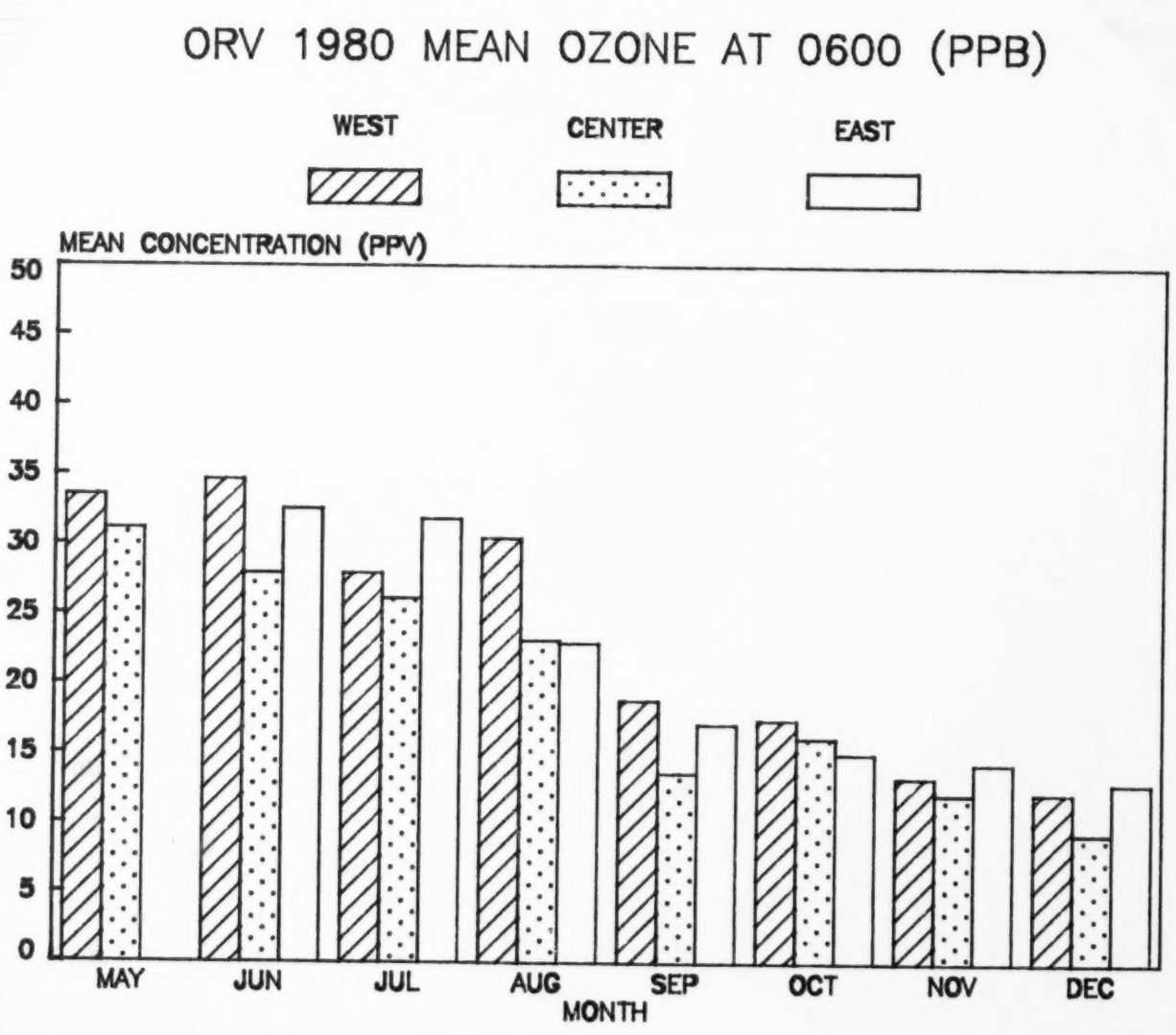


Figure 4-10. Average ozone concentration at 0600 h by month for each station.

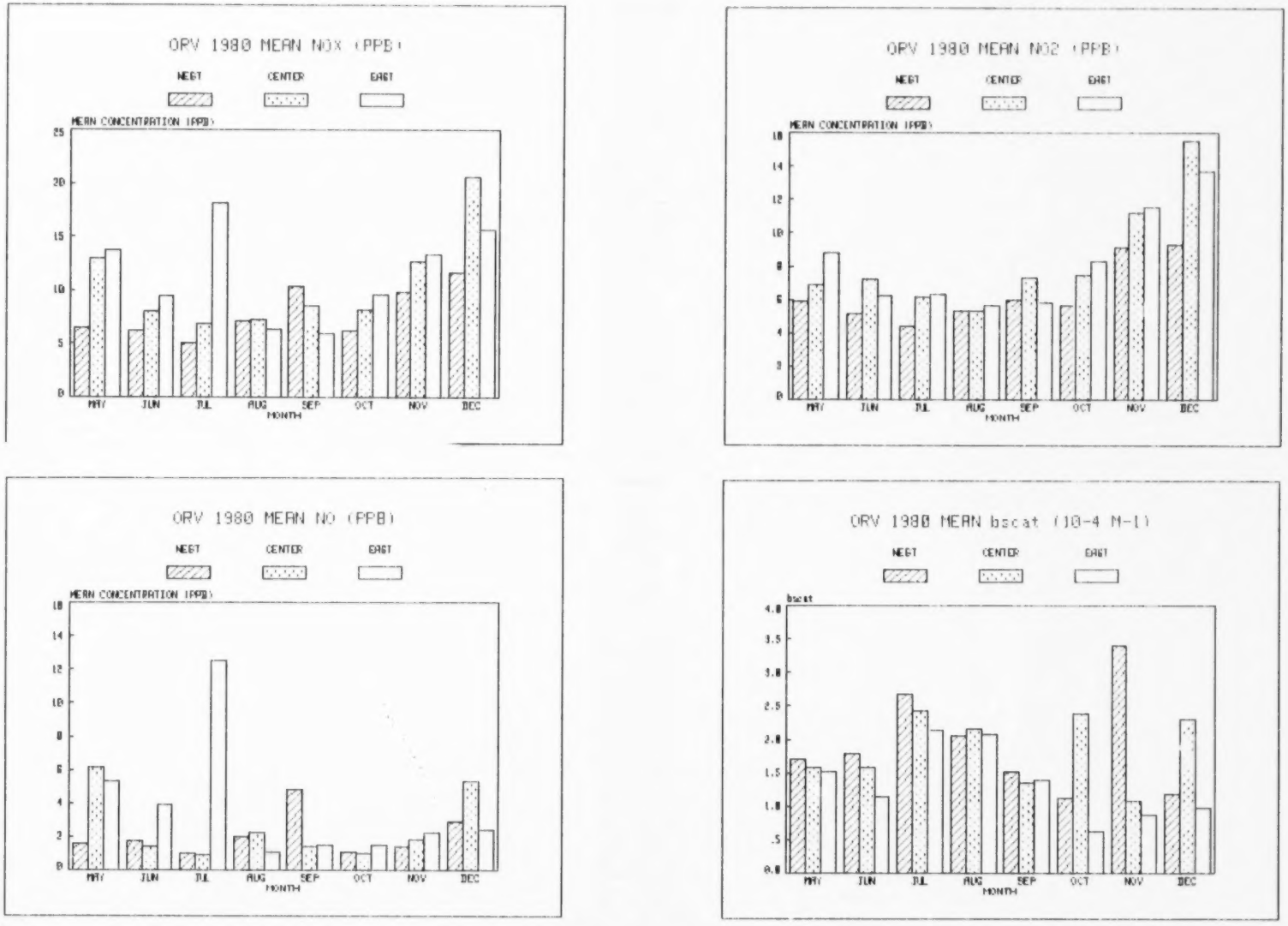


Figure 4-11. Average values for NO_x, NO, NO_2, and b_{scat} by month for each station.

TABLE 4-9. AVERAGE VALUES FOR SO_2, NO, NO_2 AND b_{scat} AND THE PERCENT DATA RECOVERED BY MONTH FOR EACH STATION

Variable, Month	Average Value, Percent Data Recovered					
	West		Center		East	
SO_2	ppb	%	ppb	%	ppb	%
May	7.9	12	6.0	85	6.5	53
June	6.7	85	5.8	82	3.3	79
July	4.3	15	6.1	86	4.0	92
Aug.	7.8	71	7.2	97	4.4	86
Sept.	8.7	92	7.6	93	6.4	87
Oct.	5.5	95	7.8	86	5.7	92
Nov.	8.6	94	11.4	85	9.1	92
Dec.	12.3	91	14.3	93	16.0	91
May-Dec.	8.2[a]		8.3[a]		7.0[a]	
NO	ppb	%	ppb	%	ppb	%
May	1.6	95	6.1	97	5.3	55
June	1.7	95	1.4	95	3.9	93
July	1.0	54	0.9	86	12.5	70
Aug.	2.0	80	2.2	96	1.1	85
Sept.	4.8	66	1.4	74	1.5	92
Oct.	1.1	92	1.0	84	1.5	92
Nov.	1.4	94	1.8	75	2.2	95
Dec.	2.9	90	5.3	38	2.4	91
May-Dec.	2.0[a]		2.4[a]		3.5[a]	
NO_2	ppb	%	ppb	%	ppb	%
May	5.9	95	6.9	97	8.8	55
June	5.1	95	7.2	96	6.2	94
July	4.4	54	6.1	86	6.3	72
Aug.	5.3	80	5.3	96	5.6	85
Sept.	6.0	66	7.3	74	5.8	92
Oct.	5.6	93	7.5	84	8.3	92
Nov.	9.1	94	11.2	75	11.5	95
Dec.	9.3	90	11.5	38	13.7	92
May-Dec.	6.5[a]		7.7[a]		8.3[a]	

(continued)

TABLE 4-9 (continued)

Variable, Month	Average Value, Percent Data Recovered					
	West		Center		East	
b_{scat}	$10^{-4}m^{-1}$	%	$10^{-4}m^{-1}$	%	$10^{-4}m^{-1}$	%
May	1.7	97	1.6	98	1.5	54
June	1.8	97	1.6	97	1.1	96
July	2.7	80	2.4	87	2.1	96
Aug.	2.1	92	2.2	97	2.1	76
Sept.	1.5	96	1.3	63	1.4	1
Oct.	1.1	96	2.4	10	0.6	48
Nov.	3.4	97	1.1	57	0.9	84
Dec.	1.2	93	2.3	66	1.0	27
May-Dec.	1.9[a]		1.8[a]		1.4[a]	

[a]Weighted by the percent of data recovered.

higher than those collected during the remainder of the averaging interval may dominate the average for that interval.

The percentages of data recovered are given in Table 4-9. Since the NO_x measurements for July at the East site cover 70% of the measurement period, the reported values cannot be biased more than 43% high because of loss of data; nor can the West or Center site values be strongly biased low.

Still to be determined is whether short-term events can account for the high NO value reported at the East site during July. We make an estimate by inspecting the daily averages and integrating under the largest peak found during the month. The integration is carried out as nearly as possible between half maxima of the peak. The percent contribution of each peak to each monthly average is computed; these data are listed in Table 4-10. During July, an

TABLE 4-10. CONTRIBUTIONS BY LARGEST EVENTS TO MONTHLY AVERAGES FOR NO, NO_2, AND SO_2 AT EACH STATION

Variable	Month	West		Center		East	
		Date[a]	% Contrib.[b]	Date[a]	% Contrib.[b]	Date[a]	% Contrib.[b]
NO	May	24(2 h)	6	24,25	51	-	-
	June	6-9	37	11,12	68	1-6	50
	July	16(2 h)	7	7	13	11-14	60
	Aug.	-	-	22,23	15	23-25	30
	Sept.	12-15	63	11	14	25	11
	Oct.	6-8	26	14	26	23	8
	Nov.	15(24 h)	17	12-14	26	17	21
	Dec.	27-29	31	-[c]	-	15,16	20
NO_2	May	1-3	18	27,28	11	-	-
	June	20-22	15	22-24	17	14,15	10
	July	23-25	19	18-20	17	3	8
	Aug.	22-24	14	17	4	22-24	16
	Sept.	23,25	15	11,12	17	27-29	16
	Oct.	30,31	11	27	9	23	8
	Nov.	26,27	12	12,13	14	17	7
	Dec.	28,29	16	-	-	27-29	21
SO_2	May	-	-	27	9	-	-
	June	20-22[d]	17	22,23[d]	20	23[d]	11
	July	-	-	7[d]	18	14-16[d]	24
	Aug.	24,25[d]	14	25[d]	15	29[d]	25
	Sept.	23-24[d]	19	11,12[d]	26	8,9[d]	15
	Oct.	29-31[e]	21	23[d]	14	23,24[d]	25
	Nov.	11,12[d]	28	20[d]	11	13,14[d]	16
	Dec.	27-29[d]	25	27-29[d]	22	27-29[d]	30

[a]Day(s) during which monthly peak concentration occurred.

[b]Percent contribution to monthly mean. If equivalent to monthly mean, then 3%/day.

[c]Data are missing for >50%.

[d]Dominated by 4-5 events.

[e]Dominated by 2 events.

event occurred during days 11 to 14 which contributed 60% of the NO detected at the East site. The July NO average is, therefore, dominated by a single, relatively short event at the East site. If one neglects this July event, however, the mean NO at the East site is 5 ppb--still significantly higher than the July values at the other sites.

The results of this major event analysis (Table 4-10) indicate that NO levels are strongly dominated by events, SO_2 levels are dominated to a lesser extent, and NO_2 levels are dominated even less. In interpreting the table, note that if each day contributed equally, the contribution per day would be 3%.

DISTRIBUTION OF SULFUR BETWEEN GAS AND PARTICLE PHASES

Monthly averages of gaseous sulfur concentrations are shown in Figure 4-12; monthly averages for fine aerosol sulfur are shown in Figure 4-13. The distribution of sulfur between gaseous sulfur and fine fraction aerosol sulfur is shown in Figure 4-14 and in Table 4-11. Those data show that from one-third to nearly one-half of the sulfur is present as fine aerosol during July and August. Less than one-tenth of the sulfur is present as fine aerosol during November and December. This distribution is consistent with expected lower rates of oxidation at lower temperatures. The total sulfur (gas and aerosol) is shown in Figure 4-15 and in Table 4-11 and is roughly constant except for a marked increase at all sites during December. A statistical analysis shows that the variance of the monthly averages for the total sulfur is 24% to 38% less than would be expected if the gaseous sulfur and aerosol sulfur were uncorrelated. In fact, they have a strong negative correlation (Figures 4-12

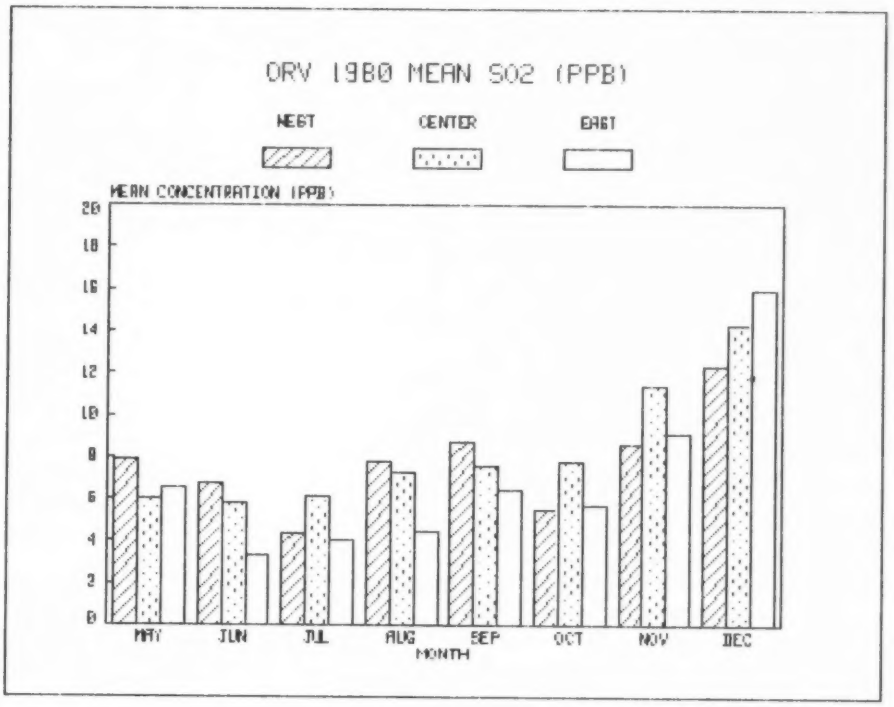


Figure 4-12. Average SO_2 concentration by month for each station.

and 4-13). We cannot detect a systematic variation of these data from site to site.

POSSIBLE SOURCES OF AEROSOL CARBON

In this section we present results of the examination of dichotomous sampler filters for carbon. Our procedure follows that of Courtney et al.[16] who analyzed aerosol composition data from Denver samples and showed that,

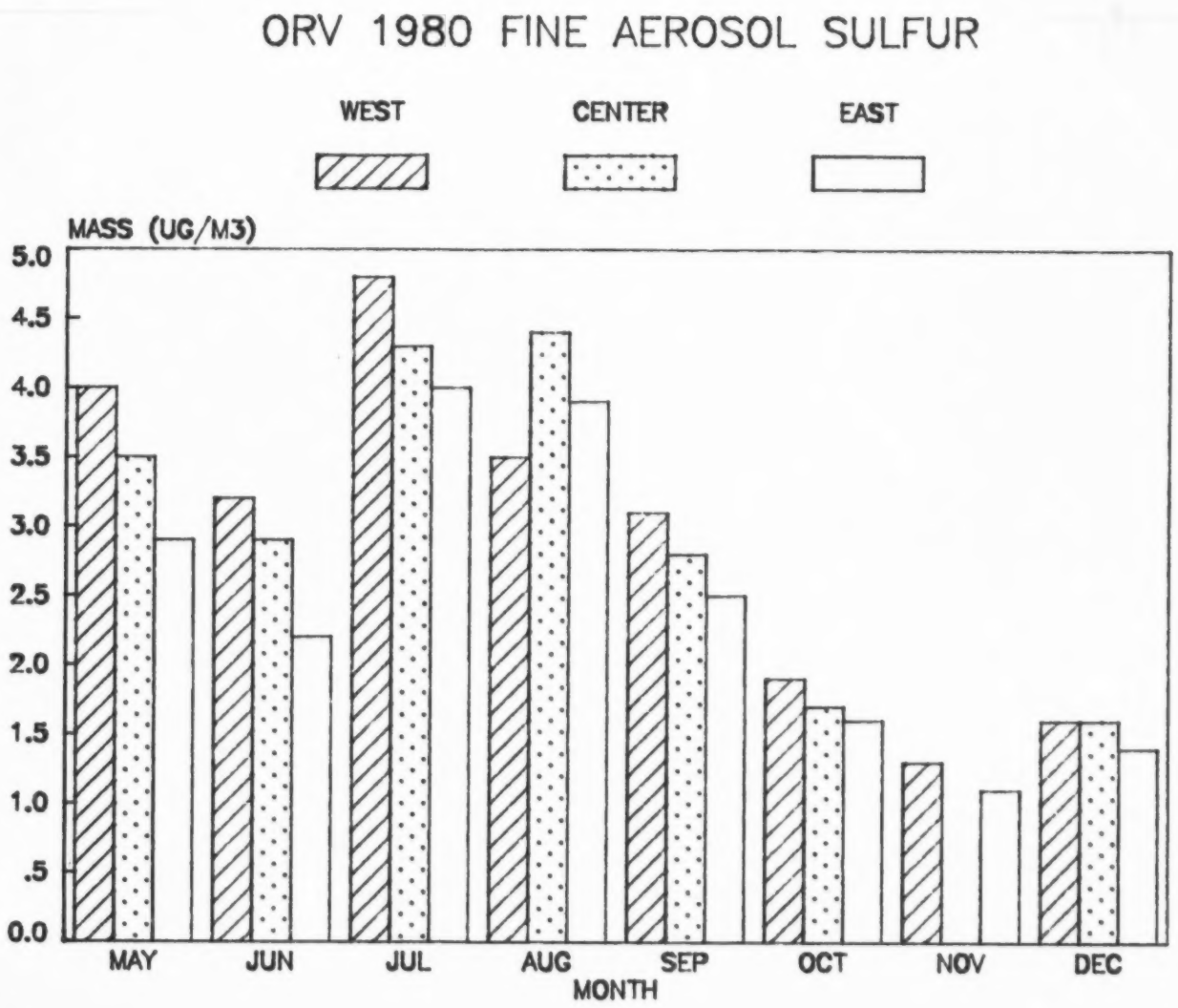


Figure 4-13. Average concentration of fine aerosol sulfur by month for each station.

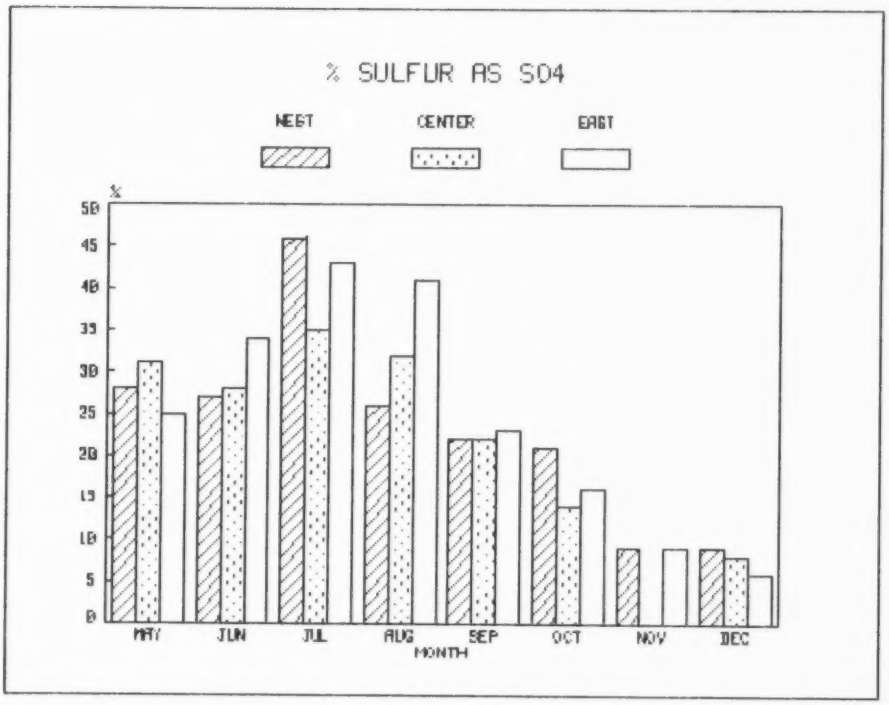


Figure 4-14. Percentage of sulfur present as $SO_4^=$ by month for each station.

TABLE 4-11. DISTRIBUTION OF SULFUR BETWEEN SO_2 AND $SO_4^=$ BY MONTH FOR EACH STATION

Month	West		Center		East	
	S as $SO_4^=$ (%)	Total S ($\mu g/m^3$)	S as $SO_4^=$ (%)	Total S ($\mu g/m^3$)	S as $SO_4^=$ (%)	Total S ($\mu g/m^3$)
May	28	14.3	31	11.3	25	11.4
June	27	11.9	28	10.4	34	6.5
July	46	10.4	35	12.2	43	9.2
Aug.	26	13.6	32	13.8	41	9.6
Sept.	22	14.1	22	12.7	23	10.8
Oct.	21	9.1	14	11.8	16	8.8
Nov.	9	12.5	-	-	9	12.9
Dec.	9	17.6	8	20.2	6	22.2
Mean		13.0		13.2		11.4

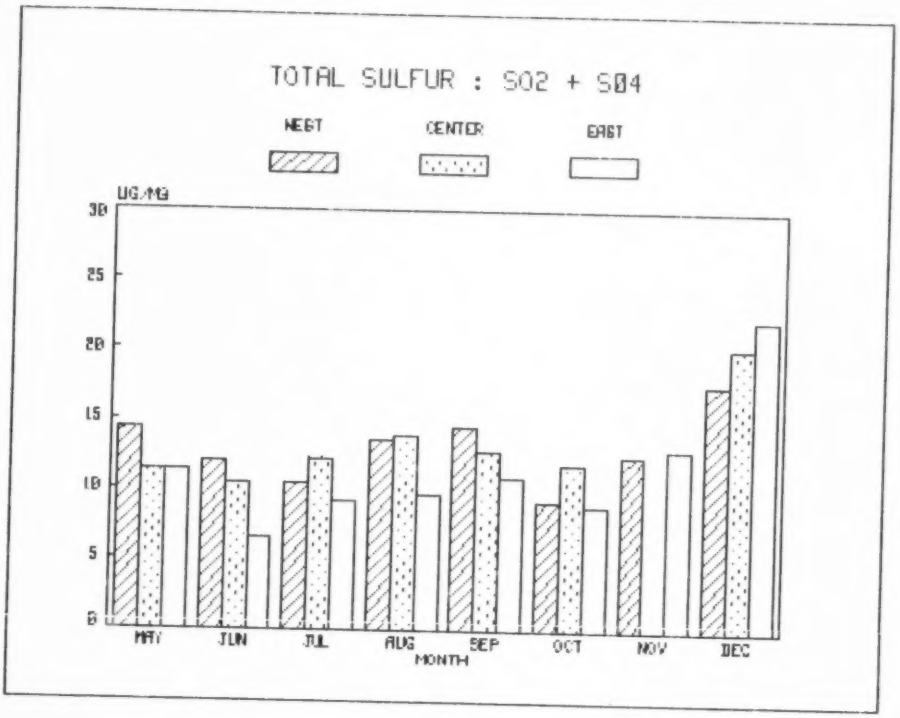


Figure 4-15. Average concentration of total sulfur by month for each station.

when the value of the elemental abundance ratio K/Fe exceeded 0.5, the light absorption coefficient of the aerosol increased (i.e., the aerosol was darker). Because light absorption has been shown to be a good estimator of elemental carbon[17] and because high potassium abundances in fine fraction aerosols occur with vegetative burning, the high K/Fe ratios observed in Denver suggested that residential wood burning had contributed carbon to the aerosol.

The fine aerosol samples collected at the ORV sites range from light to dark gray. In order to estimate relative amounts of elemental carbon, we

measured the light transmission through fine fraction aerosol samples collected at the Center station. Our dimensionless light absorption coefficient is defined as

$$b = \ln Io/I$$

where Io and I are the intensity of transmitted light through the unexposed and exposed filters, respectively. The intensity I is measured directly; Io is not measured but is inferred from its relation[17] to the unexposed filter mass density measured using beta-ray attenuation:

$$Io = 815 - 0.262\ (\beta\text{-tare})$$

where β-tare is the measured filter mass in $\mu g/cm^2$.

We performed a statistical analysis of the data from all of the fine aerosol filters for 1980 (about 300 12- and 24-h samples) from the Center site. The analysis included calculation of the correlation coefficients and multiple linear regression coefficients by least squares for the sulfur and potassium concentration, total fine aerosol mass, and light absorption coefficient. The results are given in Table 4-12. The entries in Part A show that a linear functional relationship exists to a high degree of probability between ln I/Io and each of K, K/Fe, and Mass but not S.

TABLE 4-12. CORRELATION ANALYSIS OF FINE AEROSOL COMPOSITION AND LIGHT ABSORPTION

A. Correlation Coefficients

In Io/I vs. K	0.39 ($p < 0.01$)
In Io/I vs. K/Fe	0.37 ($p < 0.01$)
In Io/I vs. Mass	0.14 ($p < 0.02$)
In Io/I vs. S	0.05

B. Multiple Linear Regression Using Average Values

In Io/I =	aS	+ bK	+ constant	
0.236 =	-0.009	+ 0.091	+ 0.154	
In Io/I =	aMass	+ bK	+ constant	
0.236 =	0	+ 0.089	+ 0.147	

In order to provide an estimate of the contributions to ln Io/I, multiple linear regression coefficients were determined from the entire data set of 300 analyses. Average values for the observations of ln I/Io, K, S, and Mass were then substituted into the regression equation with appropriate regression coefficients. The results are given in Part B of Table 4-12. We may infer that the largest contributor to fine aerosol light absorption is associated with a constant term; the next largest contributor is associated with the amount of potassium; conversely, fine aerosol mass and sulfur, by themselves, do not contribute significantly to light absorption.

One might assume from these results that elevated potassium levels in fine aerosols collected at the Center station are associated more with vegetative burning (e.g., residential woodburning), which produces relatively large amounts of carbon, than with coal-burning power plants, which are designed to burn the carbon efficiently. A limited examination of filters using optical microscopy suggests that this assumption is not correct in all cases.

We selected for microscopic examination the filters which were highest and lowest in K and those giving highest and lowest values for ln Io/I. Although our correlation analysis (described above) shows that a significant positive correlation exists between K and ln Io/I, the few filters with extreme (high and low) values for K did not also have extreme values for ln Io/I.

The optical microscopic examination showed that filters with high ln Io/I also had considerable burn debris visible as clumps of black fibrils. Filters with high K but not very high ln Io/I showed markedly less burn debris. All these observations suggest that measurements of both ln Io/I and K are necessary (but may not be sufficient) to determine whether collected aerosol has contributions from vegetative burning or from more efficient combustion processes. High K and ln Io/I suggest vegetative burning; high K without high ln Io/I suggests more efficient combustion processes.

X-RAY DIFFRACTION OF AEROSOLS

The Center station filters that were highest in Al and Si in both the fine and coarse fractions were identified. Three sets were sent to Prof. Briant Davis of the South Dakota School of Mining and Technology for crystalline substance identification.

The results of the X-ray diffraction analysis are given in Table 4-13. These percent-by-weight values have sizable uncertainties because the sample loadings ranged only from 30 to 50 $\mu g/cm^2$. For quantitative analysis, the technique requires 200 $\mu g/cm^2$ of sample. The identifications, however, are

TABLE 4-13. CRYSTALLINE MATERIALS IN AEROSOL SAMPLES FROM CENTER STATION

Sample	Material and Fraction by Weight				
	Quartz	Calcite	Kaolinite	Dolomite	Mullite
coarse 8/5	0.33	0.37	-	0.31	-
coarse 8/17	0.24	0.19	0.32	-	0.07
coarse 8/18	0.41	0.59	-	-	

	Mascagnite $[(NH_4)_2SO_4]$	Koktaite $[(NH_4)_2Ca(SO_4)_2 \cdot H_2O]$	Kaolinite	Illite	Calcite	Quartz
fine 8/5	0.49	0.17	0.31			0.03
fine 8/17	0.31	0.23	0.20	0.24		0.02
fine 8/18	0.27	0.15	0.16	0.37	0.11	0.01

unambiguous. It is interesting that mullite, a specific marker for fly ash,[18] was observed in the sample taken on 8/17. On this day, during periods of highest wind speed, the wind direction was east.

The observation of calcite in the coarse aerosol samples is consistent with the reference to calcerous soils in the Franklin County soil survey.[8] The observations that both quartz and calcite appear mostly in the coarse fraction while kaolinite appears mostly in the fine fraction are consistent with the structural properties of these minerals--clays (kaolinite) tend to form smaller particles than do quartz or calcite. The high-weight fractions of sulfates (mascagnite and koktaite) in the fine aerosols are consistent with the high-weight fractions of sulfur measured by X-ray fluorescence. All these observations are consistent with previous work by Davis et al.,[19] who pointed out that the appearance of Ca in an aerosol sulfate mineral (koktaite) may be due to its formation in a limestone scrubber for SO_2 or as an artifact reaction

product due to the mixing of a calcium mineral (calcite, dolomite) on the collecting filter.

ABSENCE OF DIURNAL AEROSOL PATTERNS

During the first several months of data collection, the dichotomous samplers were operated on 12-h sampling schedules (change at midnight and noon). Results of the evaluation of fine and coarse aerosol mass data from the period May 14 to August 14 are given in Table 4-14. These data show close agreement of the mean mass values for the two sampling periods for both aerosol fractions at all sites. In addition, the shape of the mass distributions as indicated by the medians, ranges, and percentiles are also quite similar. Based on these results, in mid November 1980 the sampling schedule was changed from 12- to 24-h periods that began at midnight.

AEROSOL SULFUR SPECIATION

A report on the analysis of aerosols using the particulate sulfur analyzer is included as Appendix A of this report. Briefly, analysis showed that, for the period December 15 to 28, an average of 6.8 $\mu g/m^3$ of sulfate was detected of which 2.9 $\mu g/m^3$ was refractory or nonvolatile. No sulfuric acid was observed; uncertainty of sulfuric acid determinations was ± 2 μg $SO_4^{=}/m^3$.

Measurements with the particulate sulfur analyzer agree with the aerosol sulfur determinations obtained by X-ray fluorescence analysis of dichotomous samples. Figure 4-16 is a histogram of aerosol sulfur during the period

TABLE 4-14. AEROSOL MASS ($\mu g/m^3$) DURING 12-H PERIODS, MAY 14 TO AUGUST 14

Station	Fraction	Mean		Median		Range		Mid Range		25% Percentile		75% Percentile	
		Mid-night	Noon	Mid-night	Noon	Mid-night	Noon	Mid-night	Noon	Mid-night	Noon	Mid-night	Noon
West	fine	27	27	26	27	71	77	40	38	16	17	35	34
	coarse	13	17	12	16	40	58	18	30	9	11	17	24
Center	fine	22	25	21	24	50	59	28	33	11	14	29	36
	coarse	10	15	9	14	29	49	11	23	4	6	14	21
East	fine	23	23	19	21	83	52	47	32	14	15	28	28
	coarse	8	8	7	7	30	31	15	14	3	4	10	10

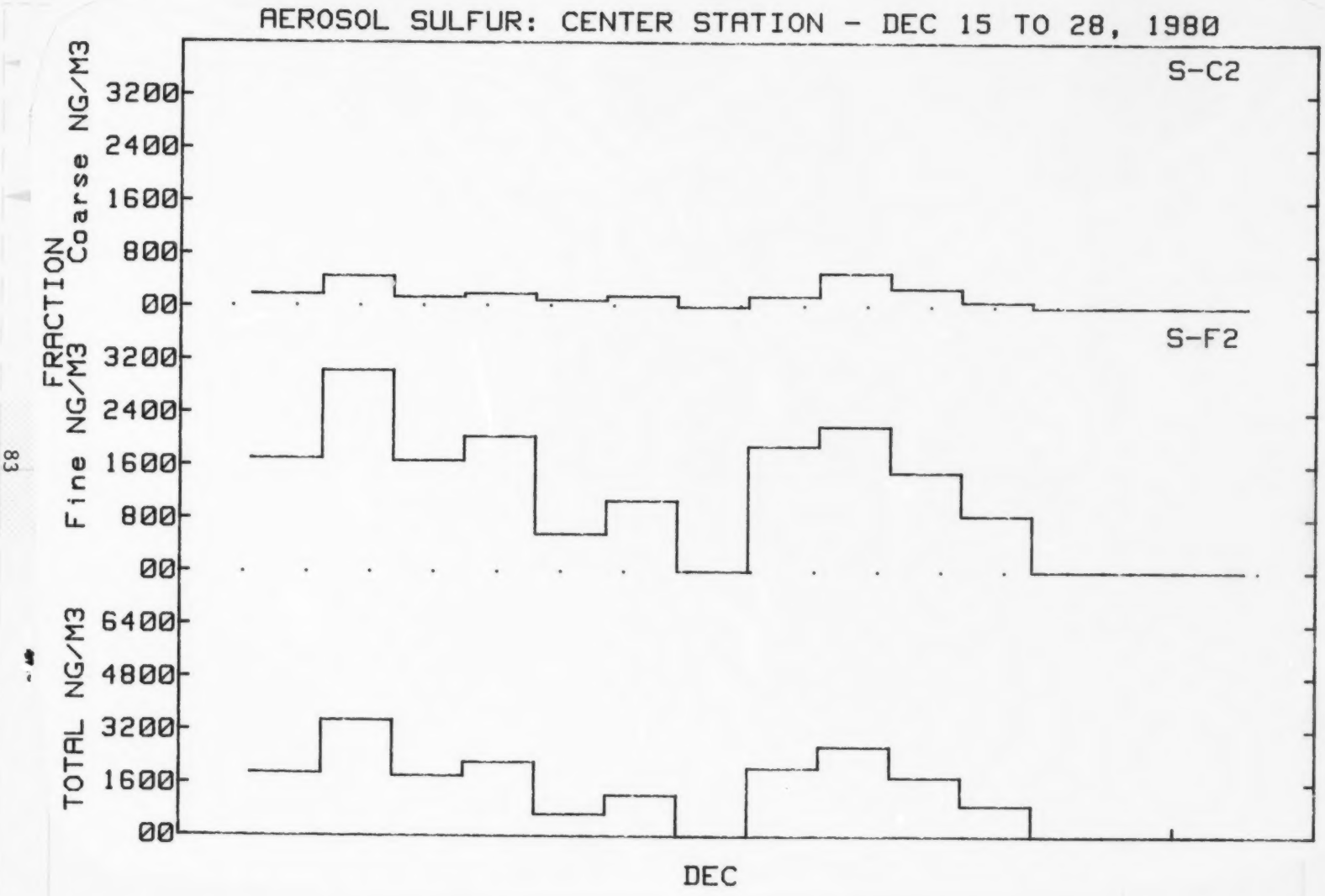


Figure 4-16. Aerosol sulfur at Center station, December 15 to 28, 1980.

December 15 to 28. The samples for December 21 and 26-28 are missing because of sampler failure. Except for missing values, all the features in the large-scale structure of the particulate sulfur analyzer are reproduced in the dichotomous aerosol sulfur data. The absolute amounts of total aerosol sulfur are in good agreement for the two techniques. The observations of both volatile and refractory sulfate using the particulate sulfur analyzer are also consistent with the X-ray diffraction analysis, which identified (for a different time period, however) large amounts of both volatile ammonium sulfate and nonvolatile calcium sulfate in the fine aerosol fraction.

THE AEROSOL CHLORINE EVENT

A remarkable increase in chlorine found in the fine fraction aerosol occurred during December 19 to 21 at all three stations. The fine aerosol chlorine concentrations (ng/m^3) at the Center station during the period May to December are shown in Figure 4-17. Days are indicated in Julian notation.

This chlorine increase was also observed simultaneously at a number of other locations in the Central and Eastern United States. Detailed analysis of aerosol composition and long-range atmospheric trajectory calculations lead us to suggest that this unusual event was due to the passage of maritime air from the far North, across Canada, and into the observation region.[20]

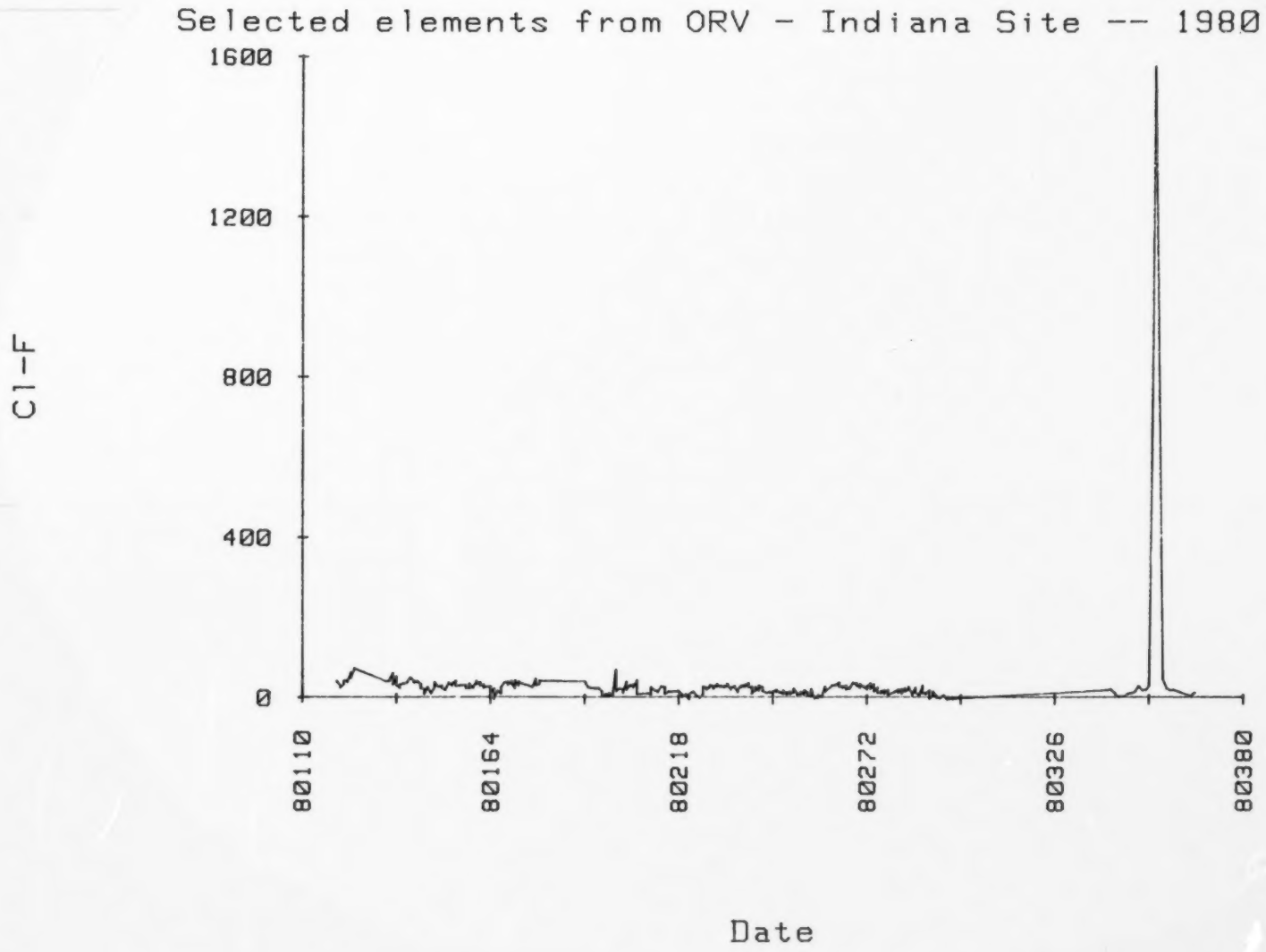


Figure 4-17. Fine aerosol chlorine at Center station.

THE FOREST FIRE

As mentioned in Section 3, a forest fire occurred in Kentucky during mid November 1980. Figures 4-18 and 4-19 present East station data for fine-fraction aerosol composition; 24-h averages for NO_x, O_3, and SO_2; and 24-h averages for the scattering coefficient. Although the East station was hundreds of kilometers from the forest fire, fine aerosol mass, sulfur, and potassium increased by factors of 10, 3, and 5, respectively. Fine aerosol iron did not increase. This pattern is consistent with our comments in previous sections concerning vegetative burning.

The NO_x and O_3 concentrations showed slight increases during the forest fire period, but NO_x showed a much larger increase several days later. The SO_2 concentrations increased by about a factor of 5. The scattering coefficient increased by more than a factor of 10.

PEROXYACETYL NITRATE

Measurements of PAN began on September 10 at the West and Center stations and on October 1 at the East station. At the West and Center stations, samples were analyzed every hour from 0700 to 1600 except on weekends. At the Center station, samples were analyzed every hour from 0000 to 2300 7 days a week, except for weekly calibration. Because of maintenance and repair problems, the data recovery was much lower for PAN measurements than for the other measurements. Below is shown the percent data recovered based on 10 measurements/day for

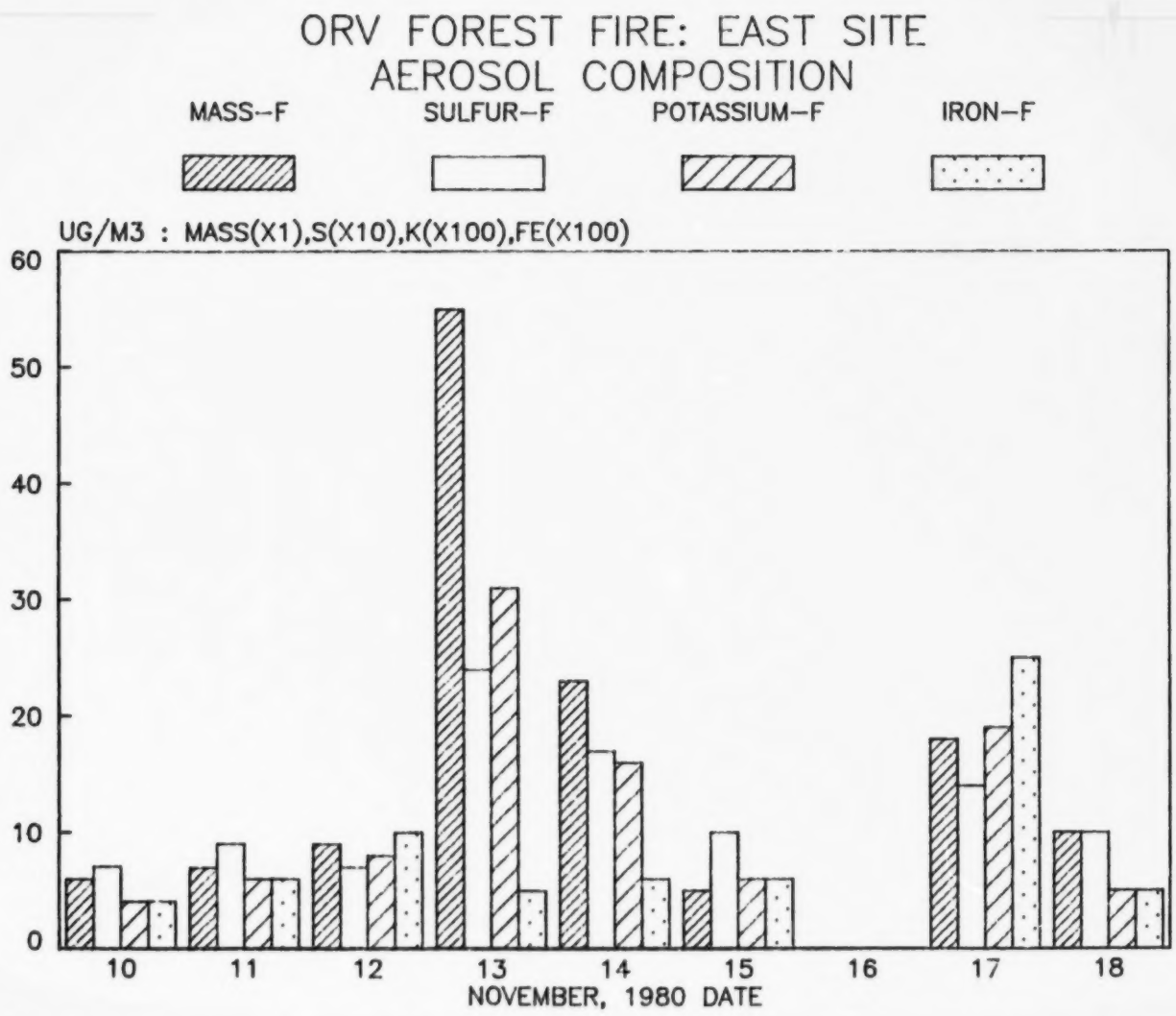


Figure 4-18. Aerosol mass and composition at East station for November 10-18, 1980. Kentucky forest fire occurred on November 13-14.

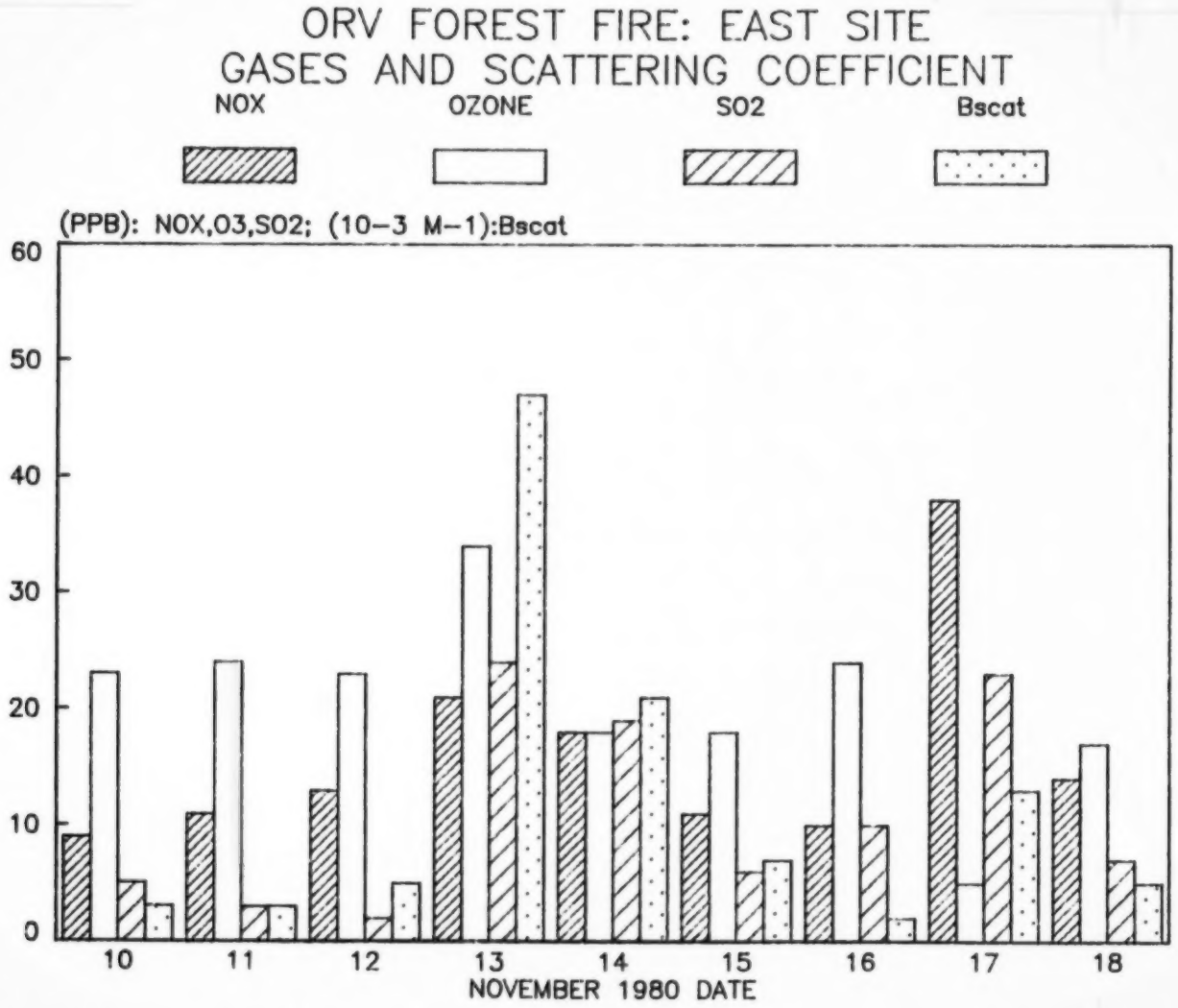


Figure 4-19. Gas concentrations and scattering coefficient at East station for November 10-18, 1980. Kentucky forest fire occurred on November 13-14.

22 days/month for the East and West stations and 24 measurements/day for 22 days/month for the Center station:

Station	Month			
	Sept.	Oct.	Nov.	Dec.
West	54	82	75	50[a]
Center	100	100	82	100
East		52	45	30

[a]On 8 days, measurements were taken through 2200.

Based on the calibration procedures and a special series of PAN audits carried out by Battelle Columbus Laboratories during the summer of 1981, we estimate the detection limit for PAN at the ORV stations to be about 0.4 ppb. Assuming this estimate to be correct, the levels of PAN measured at the stations during 1980 never exceeded 0.5 ppb. A future analysis of data not yet available may permit this estimate to be revised downward.

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